~1930

INORGANIC SEMINAR - Chemistry 105a

October	3	Hughes	Superconductivity
	10	Madson	Sols of hydrous oxide of Beryllium
	17	Jukkola	Corrosion and Passivity
	24	Meints	Inorganic Catalysts in Industry
	31	Reed	Non-aqueous solvents
November	7	Hopkins	New Tools for Research
	14	Pearce	Geochemistry
	21	Reedy	Modern Application of the Phase Rule
December	5	Ward	Reactions between solids
	12	Hayden Hardy	Isomeric Inorganic Compounds Colloidal Ice
	19	Peirce	Electrolytic Methods of Plating Metals
January	9	Stillwell	Electrodeposition of alloys
	16	Bailar	Parachor
	23	Bartow	Intermetallic compounds

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2-10-34	Production of Low Temperatures	Dr. Quill
2-17-34	The Rare Metals	Mr. Nicholson
2-24-34	Triatomic Hydrogen	Mr. Thurston
3-3-34	Chemistry of the Alkali Amides	Miss Lawrenz
3-10-34	The Amphoteric Nature of Metallic Hydroxides	Mr. West
3-17-34	Sulfur Monoxide	Mr. Huffman
3-24-34	The Single Electron Linkage	Mr. Gibbs
4-7-34	The Positive Electron	Mr. Ritchey
4-14-34	The Neutron	Mr. Lohse
4-21-34	Isopoly acids (Sulfur)	Mr. Naeser
4-28-34	Isopoly acids (Cr and Mo)	Mr. McCarty
5-5-34	Thesis	Mr. Scribner Mr. Stiegman
5-12-34	Thesis	Mr. Reed
5-19-34	Thesis	Mr. Balthis

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Feb. 9	Virginia Bartow:	Relationship of Chemistry to Social and Economic History
	L. R. Scribner:	Radioactivity of the Rare Earths
Feb. 16	L. F. Audrieth:	Theories of Ionizations & Theories of Acids, Bases & -
	E. H. Huffman:	Radioactivity of the Alkali metals
Feb. 23	J. C. Bailar Jr.:	Divalent Silver
	Margaret Lawrenz:	Present Status of the magneto optic method
Mar. 2	G. H. Reed:	Polyacids
	C. A. Stiegman:	Structure of the Complex Platinous Ion
Mar. 9	Rosalie M. Parr:	Recent Advances in the Chemistry of Selenium
	D. C. Roberts:	Isotopes of the Rare Earth Group
Mar. 16	L. L. Quill:	Origin of the Elements
	~~J. L. Gring~~ R. C. Cary:	Passivity
Mar. 23	J. H. Reedy:	The Mass Law
	J. A. Schaad:	The Oxygen Compounds of Fluorine
Mar. 30	M. J. Copley:	What Shall We Teach About Atomic Structure?
	W. J. Sparks:	Metallic Sodium
Apr. 6	B. S. Hopkins:	Origin of Petroleum
	B. C. Marklein:	~~Thesis report~~ The use of Thiurea in Analytical Chem
Apr. 13	Frank Jonelis - Thesis report	- Walden Inversion of Cobalt
	R. C. Cary:	~~University~~ Ammonia water supply
Apr. 27	Frank Birkett: - Thesis report	- Decomposition of Antiti[illegible] Use of Ammonium Sulfa[illegible]
	M. T. Schmidt: - " "	— Guanidine Salts & their Deri[illegible]
May 4	C. R. Naeser: - Thesis report	Atomic Weight of Gd; Purification of Yb.
May 11	D. H. West: - Thesis report	— Rare Earth Amalgams
May 18	C. N. McCarty: - Thesis report	— Analogies of Rare Ea[illegible] are they & their are Spect[illegible]

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Feb. 9	Virginia Bartow:	Relationship of Chemistry to Social and Economic History
	L. R. Dorfmeier:	Radioactivity of the Rare Earths
Feb. 16	L. F. Audrieth:	Uses of Isomorphous Mixtures of Acids, Bases &
	E. R. Huffman:	Reducestant of the alkali metals
Feb. 23	J. G. Dailey Jr.:	Dwelet Alloy
	Margaret Lawrence:	Great Salts of the vegets optic Method
Mar. 2	G. H. Read:	The Geiger
	G. A. Stiegman:	Structure of the Co-phin Platinum Ion
Mar. 9	Rosalie M. Fatr:	Great Discovery to Chemist of Science
	D. C. Roberts:	Isotopes of the Rare Earth Group
Mar. 16	L. L. Quill:	Origin of the Element
	~~J. L. Gaige~~:	Geochemistry
Mar. 23	J. H. Heady:	The Mass Law
	J. A. Schaad:	The Electrochemistry of Phosphorus
Mar. 30	M. J. Cooley:	What Shall We Teach About Atomic Structure?
	V. J. Sparks:	Vanadium Sodium
Apr. 6	H. S. Hopkins:	Origin of Petroleum
	S. O. Merklein:	Electrochemical Effect
Apr. 13	Frank Jonella - Thesis report	Electrochemical Measurement of Electrolyte
	H. C. Gary:	Electrolytic Water Energy of Electrolyte
Apr. 27	Frank Birkett: - Thesis report	Ion Conversion by Ion Exchange
	W. T. Schmidt: - "	" - Electrolytic Ion Exchange
May 4	E. R. Nasser: - Thesis report	Electrolytic Energy of Electrolyte
May 11	D. H. West: - Thesis report	Effect of Electrolyte
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I N O R G A N I C S E M I N A R

1936--1945

John C. Bailar Jr.

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1936-1941

H.A. Laitinen

VOLTAMMETRY (POLAROGRAPHY) AND AMPEROMETRIC TITRATIONS

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- B. Practical examples using Dropping Mercury and Rotating Platinum Microelectrode

ULTRASONIC REACTIONS

Ultrasonic waves are those sound waves having frequencies above the audible range, i. e., above 17000 cycles per second. They are commonly produced by taking advantage of the piezo-electric property of quartz or tourmaline crystals. Mechanical oscillations are stimulated in the crystal by placing it in an alternating electrical field. The vibrating system is immersed in a bath of transformer-oil and the mixtures to be investigated are placed in thin walled glass tubes which are clamped in the oil bath.

Some effects which have been observed are the following:

1) Small concentrations of H_2O_2 have been found in water saturated with O_2. When water is saturated with air, H_2O_2 and HNO_2 are found after treatment with ultrasonic waves.

2) Examples of intensive ultrasound action on passivity and activation processes include the lessened passivity of Fe in H_2SO_4, Pb in Na_2CO_3, Fe and Cr in conc. HNO_3, and hastened anodic passivity of Al and of Ni in weakly acidic H_2SO_4 solution.

3) Ultrasound waves certain reactions including the hydrolysis of dimethyl sulphate, the evolution of CO_2 by the action of H_2SO_4 or HCl on marble, and the liberation of H_2 from H_2SO_4 or HCl by Zn.

4) The molecular rearrangement of benzazide ($PhCON_3 \rightarrow N_2 + PhNCO$) is induced by ultrasonic waves.

5) Solids of low cohesion, e.g., mica, talc, gypsum, graphite, sulphur, and hematite may be dispersed in liquids by ultrasonic waves. Solid metals have not been so dispersed. However, when a plate of an electro negative metal is dipped with an aqueous solution of a metallic salt and supersonic waves are applied, the colloid of the depositing metal is obtained.

6) Detonation of NCl_3 and NI_3

7) Boiling point lowerings amounting to two degrees were found by treating CCl_4, $PhCH_3$, Et_2O, and H_2O with ultra-sound. The transition point of yellow HgI_2 to the red modification is lowered through ultrasound.

8) Depolymerization is effected by ultrasonic waves.

9) Ultrasonic waves may bring about formation of emulsions and fogs, or they may cause coagulation of a colloid.

No exact explantion as to the mechanism of reactions influenced by ultrasound has been attempted. There is, however, general agreement among theorists that cavitation phenomena resulting from the action of ultrasonic waves are in some way responsible for the effects produced. Cavitation refers to the formation and subsequent collapse of minute gas bubbles in a liquid which is subjected to a disrupting force. The collapse of these hollow spaces can bring about large ratios of energy concentration as it has been calculated that pressures of thousands of atmospheres may be developed at the moment when a cavity collapses to a small fraction of its original diameter. High kinetic energies are thus concentrated in very small regions.

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Porter and Young, J.Am.Chem.Soc., 60, 1497-500 (1938)
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Sällner, Trans. Faraday Soc., 34, 1070-4 (1938)
Sällner, J. Phys. Chem., 42, 1071 (1938)
Young and Kersten, J. Chem. Physics, 4, 436-7 (1936)

Betty Rapp

Seminar Abstract- Rhenium Reactions---- 3/17/36

1. Discovered 1925, Dr. Wm. Noddack and Dr. Ida Tacke, Berlin.
2. First produced commercially 1929 in kg. lots. Vereinigten chemische Fabriken, Leopoldshall sole producers- 1934 45 Dollars an oz.
3. Occurrence- Traces in many minerals -Molybdenite 20 p,p,m, cu refinery slime 50 p.p.m. --Cu slimes commercial source.
4. Commercial Use- Dr. Fink Electroplated Re-fine for Rh.
5. Compounds: (a) Direct: Re_2O_7, Re_2S_7, ReF_6, $ReCL_5$, $ReBr_3$, Also REO_2, $ReCL_3$, by reduction and oxy halides, (b) In solution nearly always Reo_4 or $Recl_6$, (c) Soluble HNO3 $Re + 2HNo3 -- No(ReO_4) + H_2O$, Insoluble Hel, H_2SO4. (d) Reported but questionable Re_2O_3, $Re\ CL_6$, $Re\ CL_7$, $Re\ CL_4$, $KRe\ CL_4$.
6. Since present in traces in many minerals the following analytical reactions are listed. (a) Ore in H_2 at 900degrees all Re Cpds to Redegrees, heated in air Re_2O_7 sublimes, current of SO_2 Re_2O_7---Blue (unknown composition) Definite positive but not conclusive negative test as alkalies interfere. (b) Prescott and Johnson system- Re in as ppt, Treat ppt. Na_2O_2 and identify Re as Cs or K Re O_4 microscopically. (c) Noyes and Bray system- Re in Rh- Is filtsate- careful reduction of Rh-Ir with hydrazine. Re identified as in (b). (d) Spectroscopic. Noddacks claim can detect 105/ to 10^6 pts. Re- Hurd puts limit at 2×10^5 so not useful for ores. (e) Re O_4 and Re Cl_6 separated in solin by pppt/n of Re Cl_6 by cinchonidine, mor p anisidine, tri-n Omyl anime and several other organic bases, both ions ppt/d. by nitron, brucine, flairne, etc. bases. (f) Colonmetric- (1) Re O_4 Hel, sn Cl_2 / CNS Brown-

MO Interferes Remove Mo as Xanthate in CH CL_3, then Re test.
(2) REO_4 Sn Cl_2 yellow (Small amt. RE) 100° Green: Red (large

~~K_4 (Fe Cn)$_6$~~ dimethylglyoxime.

amount(100° green Flourescence.
(G) Quantitative--ppt. Re as Re_2S_7 by Na_2S and $Na_2S_2O_3$
Redissolve ppt. Na_2O_2- Re ppt. by nitron acetate-weigh

References(Hurd-Ind. and Eng. Chem. (oval. Ed.) 8,11, (1936)
Sammakung Chemisches and chemische technische Vostrage N.S. 11 (1932)

Bnt. Ann. Reports-XXXl, 123, (1934)
Fink and Peren, Trans. Electrochem. Sec. 66 381 (1934)

J.P. Mc Reynolds.

$$4Re + 14HNO_3 \rightarrow 4NO\,ReO_4 + 7H_2O + 10NO$$

CONSTITUTION OF WATER IN DIFFERENT STATES. 3/24/36

I. Ramakrishna Rao, M.A. P.H.D., Andhra University, Waltair. Royal Society of London. proceedings. 145 Series A, 489, 1934.

I. The Nature of Raman spectra.

A. When an intense beam of monochromatic light is scattered by a pure liquid the scattered light always contains the original frequency in comparatively great intensity, together with a small quantity of scattered light of lower frequency.

B. The difference in frequency between the incident beam and the scattered beam of light corresponds to a directly observed frequency in the infra red region for the substance being observed.

II. The application of Raman spectra to the study of the constitution of Water.

A. Experimental details.

1. Apparatus used for obtaining Raman spectra of ice.
2. Modifications of apparatus for Water at other temperatures.

B. Results of experimentation. The following facts make it necessary to assume the presence of three types of molecules in Water.

1. In the liquid state there are three components of the band with Raman frequencies equal to 3216, 3435 and 3582 cm^{-1}.
2. Water Vapor gives rise to a single sharp Raman line.
3. Ice reveals only two components with Raman frequencies equal to to 3196 and 3321 cm^{-1}.
4. The systematic variations in the intensity of these bands with change of state and temperature cannot be explained except on the hypothesis of the existence of three types of molecules whose relative proportions vary with changes of state.

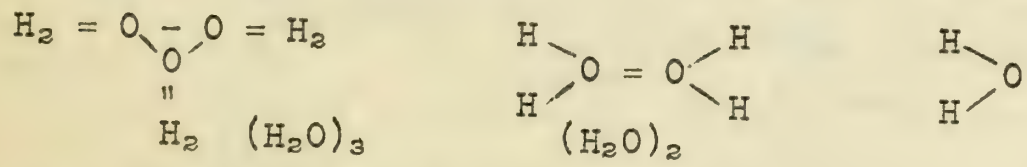
III. Relative intensities of the 3 components of the Water band as determined from an analysis of the intensity curves.

A. Number of single or vapor molecules progressively increases in intensity with increasing temperatures.

B. Number of Water or double molecules remains practically constant except in the transition from ice to water at 0°C where there is a sudden increase. They appear to be maximum at 4°C.

C. Triple or ice molecules suddenly diminish in number from ice to water at 0° C. and then gradually diminish with increasing temperature.

IV. Graphic formulas proposed for the three Water Molecules.



V. Other factors lending support to the hypothesis that water is composed of mono-di- and tri hydrol.

A. Biological effects of recently melted, as compared with recently condensed water.

B. Exhaustion of ice-forming power of water after removal of ice at uniform intervals.

C. Difference in rate of freezing of ice and steam water.

B. S. Marklein

The Nature of the Metallic State

March 31, 1936

W. C. Fernelius and R. F. Robey--J. Chem. Ed., 12, 53 (1935)
J. D. Bernal--Trans. Faraday Soc., 25, 367 (1929)

I. Properties which must be accounted for by any complete theory of the metallic state:
   A. Metallic luster.
   B. High thermal conductivity.
   C. High electrical conductivity without material transfer.
   D. Thermionic, photoelectric, and other effects.
   E. Malleability and ductility.

II. Electron gas theories of the metallic state.
   A. Classical theories:- Qualitatively successful, but required a higher electron energy than the classical theory could afford.
   B. Quantum treatment:- the electron gas is degenerate.

III. Solutions of metals in NH_3
   A. $Me \xrightarrow{NH_3} Me^+ + e^-$
   B. Concentrated solutions possess metallic characteristics. Dilute solutions are electrolytic.
   C. Volume relations in $Na-NH_3$ solutions.

IV. Metallicity is not an atomic property.
   A. It is due to a state of aggregation.
   B. The presence of "free" electrons will account for points under IA, IB, IC, and ID.

V. Crystal structure of the elements.
   A. Class I--All A-subgroups, transition elements, and the noble metals.
      Structure--Face centered cubic, body centered cubic, and hexagonal close-packed.
   B. Class II--Group IIB, B, Al, In, Tl, and Pb
      Structure--Same types as Class I but slightly modified.
   C. Class III--C, Si, Ge, Sn, Ga, As, Sb, Bi, Se, Te, Po, I
      Structure--Such that the number of nearest neighbors is 8-N, where N is the periodic group number.
   D. Crystal structure and mechanical properties.

VI. Solid solutions, intermetallic compounds, and other metallic compounds.
   A. Effect of alloying on physical properties.
   B. α, β, and γ phases -- Perlitz' calculation.
   C. Rules governing the metallicity of compounds.
      1. With a given non-metal, the nobler the metal the more metallic the compound.
      2. With a given metal, the less active the non-metal, the more metallic the compound.
      3. The greater the complexity of the negative radical, the more metallic the compound.

Ben Briggs

INORGANIC SEMINAR April 7, 1936

RECENT CONTRIBUTIONS OF SOIL SCIENCE TO BASE EXCHANGE

J. R. Skidmore

1. Discovery in 1850 by Sir Thomas Way

2. The Importance of Base Exchange in Soils
   A. Brief review of soils with respect to formation, age, and characteristics.

3. Nature of Materials exhibiting Base Exchange properties.
   - Natural materials
     - minerals
     - organic matter
   - Artificial materials
     - Resins
     - permutite

4. Methods of Studying Soil Colloids.
   A. The nature of Soil Colloidal material.
   B. Separation or Fractionation.
      1) Electrophoresis
      2) Sedimentation (super centrifuge, etc.)

5. Methods of Studying Base Exchange.
   A. Ion exchange (Lyotrophic series).
   B. Electrodialysis
   C. Water relationships
      - Crumb formation
      - Water absorbing capacity
      - "Water of constitution"
   D. Miscellaneous
      - Freezing point lowering
      - Other liquids adsorbed
      - PH and other "acidity" measurements.

6. Theoretical
   A. Alumina tetrahedron - a structural explanation from crystal structure data.
   B. Mineral destruction by hydrogen ion replacement

7. Brief note from the Illinois College of Agriculture on base exchange minerals, and their identification - relating Base Exchange to clay mineral identification.

INORGANIC SEMINAR - April 21, 1936

A. Seifert

The Use of the Polar Molecule Concept in the Explanation of Chemical and Physical Phenomena

I. Electrovalence and Covalence
   A. Definition
   B. Rules for predicting nature of linkage
      1. Covalent molecules result when the positive ion is small with a high charge and the negative ion is large with a high charge.
      2. Electrovalent molecules result under the reverse conditions.
II. Dipoles and Dipole Moments
   A. Temporary and permanent dipoles
   B. Zero dipoles
III. Determination of molecular configurations
   A. Position of electrons
   B. Position of atoms
IV. Coordination
   A. Necessary factors for coordination
      1. One group with an unshared pair of electrons and one group short one or more pairs.
      2. Both groups polar with relatively high dipole moments
      3. Relatively low molecular weights, as a general rule
   B. Solvation
V. Association
   A. Not stoichiometrical
   B. Influence on boiling points
VI. Solubility
   A. Liquids of high dipole moment
      1. Excellent solvents for ions
      2. Good solvents for polar covalent compounds
      3. Poor solvents for compounds of zero dipole moment
   B. Mutual solubility of non-polar liquids if zero moment is not the result of widely separated high moments.
VII. Dependence of melting points on inter molecular on ionic forces in the lattice.
   A. Ideal non-polar molecules - van der Waals force only
   B. Covalent molecules with high dipole moments - van der Waals force and residual electrostatic force.
   C. Ionic lattice - electrostatic force.
   D. Covalence in giant molecules

References

S. J. French; J. Chem. Ed. 13, 122 (1936)
K. Fajans; "Radio-elements and Isotopes". Chaps. III and IV
N. V. Sidgwick; "Some Physical Properties of the Covalent Link in Chemistry", Chap. II.
Glasstone; "Recent Advances in Physical Chemistry" Chaps. I and III
Dole; "Principle of Experimental and Theoretical Electrochemistry" Chap. XII.

INORGANIC SEMINAR - May 11, 1936

The Equilibrium Between Nitric Oxide, Nitrogen Peroxide, and Aqueous Solutions of Nitric Acid

I. Important reactions in preparing HNO_3.

[1] $2NO + O_2 \longrightarrow 2NO_2$

[2] $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$

II. Determination of K for reaction [2]
  A. Dynamic method (Burdick and Freed)
  B. Static method (Abel, Schmid, and Stein; Chambers and Sherwood)

III. Comparisons of methods
  A. Dynamic method - doubtful equilibria
  B. Static method - positive check on equilibria

IV. Comparison of values of K as found:
  A. Agreement of Chambers and Sherwood with Abel, Schmid and Stein
  B. Burdick and Freeds' values low

References:

Chambers and Sherwood, J.A.C.S., 59, 316 (1937)
Burdick and Freed, J.A.C.S, 43, 518 (1921)
Taylor, Industrial and Engineering Chemistry, 17, 633 (1925)

D. F. Peppard

I Theoretical significance

The volatile carbonyls represent a type in which the metal atom takes on the number of electrons necessary to reach the atomic number of the next inert gas.

Effective atomic no: Total own & shared. Transition stable when E.A.N = next ~~regular~~ gas at. no.

II Importance of the discovery of the hydrides of the carbonyls

$Ni(CO)_4$ has the saturated inert gas structure.: $Co(CO)_4$ lacks one electron which is furnished by H in $Co(CO)_4H$. Other hydrides are known. All are unstable and very volatile.

III CO and the mode of co-ordination

Theory and evidence point to the structure $:C\ddot{\times}\times\overset{\times}{\times}O\overset{\times}{\times}$ or $\bar{C}\equiv\overset{+}{O}$
It is also suggested that the two forms $C\equiv O$ $C=O$ are in resonance with the former predominating.

Co-ordination probably takes place through the carbon $M \leftarrow \bar{C} \equiv \overset{+}{O}$ or $M^{-} - C \equiv {}^{+}O$

IV Complex carbonyls

Some regularity in composition is shown. For a molecule of type $M_x(CO)_y$ the relation holds: $G - \frac{1}{x}(xm + 2y) = x - 1$

where G = at. no. of next inert gas, m = at. no. of metallic atom. Assuming further co-ordination with the oxygen as donar to give each metallic atom a saturated structure the number of such extra bonds is easily found. With one, two and three bonds the structures are linear, triangular and tetrahedral respectively.

V Nitrosyl compounds and structure of NO

These analogous compounds are formed from nitric oxide. NO co-ordinates by contributing three electrons. Proposed structures are $[:N\cdot\times\overset{\times}{\times}O]^{+}$ $N\equiv\overset{+}{O}$ $\bar{M} - \overset{+}{N} \equiv \overset{+}{O}$

Manchot

W.J. Peppel

$Fe(CO)_5 + HgSO_4 + H_2SO_4 \rightarrow Fe(CO)_4Hg$ or $\xrightarrow[NH_3]{Hg} Fe(CO)_4X_2$

$Fe(CO)_5 + Ba(OH)_2$ (or $MgCl_2 + H_2O$) $\rightarrow Fe(CO)_4H_2 + BaCO_3$; $Co(CO)_4 + OH^- \rightarrow 2CO\cdot(CO)_4H + CO_3'' [Co(CO)_3$

$Fe(CO)_4H_2 \xrightarrow[\Delta]{H^+} Fe(CO)_5 + [Fe(CO)_3]_x + H_2$ no hydride $Ni(CO)_4$

	$Ni(CO)_4$	$Co(CO)_3(NO)$ (?)	$Fe(CO)_2(NO)_2$
B.P.	43°	78.6	110°

Bill Structure Study.

$Ru + CO \xrightarrow[\text{expr.}]{300°}$ $CrCl_3 + CO + \text{Estrigon}$? $\xrightarrow{\text{Pow.}}$

$K_2[Fe(CN)_5NO] + S^{=} \rightarrow K_4[Fe(CN)_5NOS]$

$-N\equiv O + S^{=} \rightarrow -N=O$ (S)

$-N\equiv O + O^{=} \rightarrow -N=O$ (O)

:S: 2 electrons out

:N::O: Nos from metal

Z. anorg. Chem. 221, 321-53 (1935)
226, 385-406 (1936)

Proc. Roy. Soc. (1934)(A) 144 521.

Naturwiss. 19, 360 (1931)

INORGANIC SEMINAR 10/6/1936

Sonic Activation in Chemical Systems

1. Earlier effects observed in ultra-sonic cavitation
   (a) $H_2O + [O] \longrightarrow H_2O_2$
   (b) $X^- + \underset{air}{[O]} \longrightarrow XO^- \longrightarrow X_2$
   (c) $H_2S + \underset{air}{[O]} \longrightarrow H_2O + S$
   (d) Dissolved air essential
   (e) Cavitation apparent source of activation

2. Sonic caviation effects
   (a) $H_2O + [O] \longrightarrow H_2O_2$
      (1) Chemical Change per unit energy independent of frequency
      (2) No evidence of O_3 formation
   (b) $NaHSO_3 + [O] \longrightarrow NaHSO_4$
      (1) Rate of formation too great to be due to reaction $NaHSO_3 + H_2O_2 \longrightarrow NaHSO_4 + H_2O$
      (2) Rate of formation affected by amount of agitation, probably due to rate of renewal of O_2 in solution
   (c) $Cl^- + [O] \longrightarrow ClO^-$ (Traces of ClO_3^-)
      (1) Reaction $Cl^- + H_2O_2 \longrightarrow ClO^- + H_2O$ goes but will not account for all ClO^- formed
   (d) $CCl_4 + [O] \longrightarrow Cl_2 + Cl^- + ---$
      $CHCl_3 + [O] \longrightarrow Cl_2 + Cl^- + ---$
   (e) Chemical luminescence - An H_2O solution of "luminon" when cavitated gave off light. (H_2O_2 and another oxidizing agent necessary)

3. Due to lack of refinement of apparatus and to lack of quantitative means of estimation the degree of cavitation only a tentative theoretical explanation can be advanced, namely, excitation or ionization of the gas dissolved, in this case oxygen.

Flosdorf, Chambers and Malisoff - J. Am. Chem. Soc. 58, 1069-76 (1936)

J. P. McReynolds

Inorganic Seminar Report - October 14, 1936

1. Preparation of Hexametaphosphate: (1) heating $NaPO_3$ or (2) $Na_2H_2P_2O_7$ to 700°.

2. Methods of analysis and Purity of the Product obtained
   1) Volumetric 99.98 % $Na_6P_6O_{18}$
   2) Gravimetric 99.98 % $Na_6P_6O_{18}$
   Loss of wt. upon ignition - .8 %

3. Solubility of various salts in HMP.
   a) Calcium. oxalate, normal phosphate, carbonate, and sulfate soluble in HMP solution.
   b) Strontium compounds behave as do the calcium materials. The sulfate is slowly soluble in H.M.P.
   c) Barium chromate and sulfate will not precipitate in a solution containing H.M.P. at ordinary temperatures. If the materials ($BaSO_4$ and $BaCrO_4$) are added to a solution of H.M.P. no solvent action is noticed. Barium oxalate and barium phosphate behave as do the similar calcium compounds.
   d) $Mg_3(PO_4)_2$ is soluble in H.M.P. but reprecipitated upon addition of NH_4OH; excess of H.M.P. does not form a ppt. when added to $Mg_3(PO_4)_2$. $MgCO_3$ behaves similarly to $CaCO_3$.
   e) $FeCO_3$ and $Fe(OH)_2$ do not ppt. in H.M.P. solution. The color becomes dark green in color but no ppt. is noted.

4. Theory of the action of H.M.P.: One atom of dibasic metal replaces two of sodium in the H.M.P. forming a stable material.

5. Activity of H.M.P. is related to solubility data:

6. Action of H.M.P. on trivalent and amphoteric divalent elements.
   a) $Fe(OH)_3$ was held in solution to the extent of 253 mg. By 1 gm. of H.M.P. $Fe(OH)_3$ ppted upon addition of NH_4OH to this solution.
   PPted $Fe(OH)_3$ is but very slightly soluble in H.M.P. - Two atoms of Fe are absorbed by H.M.P. moledules. No explanation for the mechanism is offered.
   b) $Al(OH)_3$ behaved as did $Fe(OH)_3$
   c) $PbCO_3$ and $ZnCO_3$ - of these two dibasic carbonates about 1/3 and 1/2 (respectively) of the metallic ions were held in solution by the H.M.P. Here again no theory is postulated.
   d) Action on Portland Cement - detailed tables of these data will be given

7. Stability of H.M.P. in laundry waters.

D. G. Nicholson

We	They
	50
	30
	90
	8
165	

We	They
	75
	500
	25
	100
	100
50	100
30	30
120	160
	60
	70
	360

Oct 20, 1936

SOME REACTIONS OF GALLIUM-ORGANO AND GERMANIUM-ORGANO COMPOUNDS IN LIQUID AMMONIA.

Reference: Germanium
E. A. Flood, J. Am. Chem. Soc. 55, 4935-4938 (1933)
Brownw.

I.a) Ethyl germanium triodide can be prepared according to the reaction

$C_2H_5I + GeI_2 \xrightarrow{110^\circ} C_2H_5GeI_3$. (30 to 4 day) (up to 140 GeI_4 + a gas) It is a lemon colored liquid at room temperature, but deepens slowly to a deep red as it is heated up to 250°. B.P. = 281° at 755 mm., and M.P. = -1.5 to -2.5°. It dissolves in ordinary organic solvents without apparent change.

b) An aqueous solution of ethyl germanium triiodide when boiled with Ag_2O yields $(C_2H_5GeO)_2O$, which does not hydrate to C_2H_5 GeOOH.

c) Ammonolysis of the triiodide produces C_2H_5GeN. Hydrolysis of the latter compound gives $(C_2H_5GeO)_2O$, which also does not give C_2H_5GeOOH.

White solid $\xrightarrow{300^\circ}$ no melt. $\xrightarrow[\text{vac}]{\text{higher}}$ sublimes + decomposes.

References: Gallium
C. A. Krauss and F. E. Toonder, Proc. Nat. Acad. Sci. 19 292-298 (1933)
C. A. Kraus and F. E. Toonder, J. Am. Chem. Soc. 55, 3547-3554 (1933)

II. Pure trimethyl gallium can be prepared by the action of dimethyl zinc on gallium trichloride: the reaction is practically quantitative. $2GaCl_3 + 3(CH_3)_2Zn \longrightarrow 2(CH_3)_3Ga + 3ZnCl_2$. The gallium-organo compound ammonates easily to form $(CH_3)_3GaNH_3$. The latter compound with HCl in dry ether gives $(CH_3)_2GaCl$ and CH_4.

III. The action of Na on $(CH_3)_3GaNH_3$ in liquid ammonia gives

(1) $Na + 2(CH_3)_3Ga\cdot NH_3 \longrightarrow (CH_3)_3Ga\cdot NH_2\cdot Ga(CH_3)_3^- + Na^+ + 1/2H_2$

(2) $2Na + 2(CH_3)_3Ga\cdot NH_3 \longrightarrow (CH_3)_3Ga{:}Ga(CH_3)_3^= + 2Na^+ + 2NH_3$ (+NH_3)

In a concentrated solution, only (1) takes place.

IV. In the hope that reaction (1) could be suppressed, $C_2H_5NH_2$ was tried as a solvent, but an almost identical reaction resulted.

$Li + (CH_3)_3Ga\cdot C_2H_5NH_2 \longrightarrow (CH_3)_3Ga\cdot C_2H_5NHLi + 1/2H_2$

and then a reaction exactly analogous to (2) took place.

V. $Na_2\ (CH_3)_3Ga_2$ reacts with NH_4Br to regenerate $(CH_3)_3Ga$. The corresponding Li salt decomposes with the evolution of hydrogen when the ethylamine is evaporated, and $LiC_2H_5NH\cdot Ga(CH_3)_3$ is formed.

VI. $(CH_3)_2GaCl$ is reduced to $(CH_3)_2Ga$ with Na in liquid ammonia.

October 20, 1936 Michael Sveda

$(CH_3)_3Ga{:}Na{:}Na{:}Ga(CH_3)_3 + NH_4Br \rightarrow (CH_3)_3Ga + NH_3$

distilled $C_2H_5NH_2$ H_2 evolved + $(C_2H_5)_3Ga{:}C_2H_5NHLi$

$Li_3B + KNH_2$ mixture but $Li_3B{:}NK$ stable in air

Inorganic Seminar

October 27, 1936

PURIFICATION OF CERIUM RESIDUES

Object - To obtain a suitable material for the preparation of high grade ceric salts for use as analytical reagents

I. Sources of Cerium - ores and commercial residues
II. Separation of the rare earths (general methods)
   1. Thermal decomposition (and oxidation in dry way)
   2. Oxidations in the wet way
   3. Fractional precipitation (or solution)
   4. Fractional crystallization
   5. Physical means

III. Separation and purification of cerium
   1. Basic nitrate sulfate method
   2. James bromate method
   3. Mosander chlorine method
   4. Auer V. Welsbach ceric ammonium nitrate method
   5. Drossbach permanganate method
   6. Mixed perchloric - sulfuric acids
   7. Other methods
IV. Experimental
   1. Preparation of ceric ammonium sulfate from purified ceria (88-90 CeO_2)
   2. Treatment of crude residues
      a. Purification, if soluble in HNO_3
      b. " , " insoluble in HNO_3
      c. Conversion to ceric ammonium sulfate
V. Ceric salts as analytical reagents

References

1. Basis of report - Experimental work in this laboratory
2. General - Böhm (German) 2 vol. 1904; Spencer (Eng.) 1919; Mellor, Friend
3. Cerium as anion - $[Ce(NO_3)_6]^{=}$ Z. anorg. Chemie 27:359(1901); Atti R. Accad. Lincei [V] 16: 395 (1907) $[CeO_3]^{=}$ Naturwissenschaften 22:20b (1934)
4. Analytical uses - Furman in Margosches "Die Chemische Analyse, Vol. 33 neuere massanalytische Methoden p. 21-43

Inorganic Seminar November 10, 1936

THE CHANGE IN ABSORPTION SPECTRUM OF COBALT CHLORIDE IN AQUEOUS SOLUTION WITH INCREASING CONCENTRATION OF HYDROCHLORIC ACID.

$Co(OH)_2$ + Conc. KOH → $K_2[Co(OH)_4]$

The theory is held that both in the crystal and in solution the cobalt atom is in association with 6 other atoms or groups, when the color is red, and four when the color is blue.

1. Early work leading to such a theory.
   a) Absorption spectra of red and blue cobalt pigments.
   b) " " " " " " cobaltous compounds in solutions.
   c) Crystal structure determinations of red and blue pigments, and ability to predict crystal structure of cobalt compounds from color.
   d) Transition from red to blue has been followed by measuring densities, viscosities, refractive indices, surface tensions, and electrical conductivities.

II. Absorption spectra of a series of solutions containing the same amount of cobalt chloride, with increasing concentration of hydrochloric acid.
   1. Apparatus Used. Definition of density and of Bunsen Extinction Coefficient.
   2. Results.
      a) The extinction coefficients at the maxima of the four principal bands, 695, 666, 626, 610 mμ have been plotted against concentration of acid.
      b) Curves show that no blue constituent is formed until a critical concentration of 5 N HCl is reached.
      c) Amount of blue constituent increases rapidly with increasing concentration of acid, the relation becoming linear at 7.1 N acid, and for 695 and 666 mμ bands it is complete at 9 N acid.
      d) Ratio of relative numbers of Cl atoms to water molecules at these three critical concentrations of acid is 2:3:4:
      e) Mechanism of Change is:

$$\left[Co(H_2O)_6\right]^{++} \longrightarrow \left[Co(H_2O)_4Cl_2\right] \longrightarrow \left[Co(H_2O)_3Cl_3\right]^{-} \longrightarrow \left[CoCl_4\right]^{=}$$

      f) For the bands 626 and 610 mμ, the extinction coefficient continues to increase with increasing concentration of acid beyond 9 N. This is explained by depression of ionization of complex.

III. The change in absorption spectrum of cobalt chloride in aqueous HCl solution with change of temperature.

IV. The absorption spectrum of cobalt chloride in presence of $MgCl_2$ in aqueous solution.

References:

Howell and Jackson, proc. of Royal Society: 142 587-597, 1933
Howell and Jackson, " " " " 155 33-41, 1936
Howell and Jackson, J. Chem. Society, Sept. 1936 1268-1273

B. C. Marklein

Hill + Howell - Phil. Mag. 48, 833 (1924)
Howell - J. Chem Soc. P58, 1927
- J. Chem Soc. P2039, 1927
+ P843, 1927

Nov. 11, 1936 (?)

INORGANIC SEMINAR

R. W. Spence

BEHAVIOR OF INORGANIC COMPOUNDS IN LIQUID HYDROGEN FLUORIDE

I. Solvent power of (HF).
   A) Alkali metal fluorides soluble, alkaline earth fluorides only slightly soluble.
   B) Acids and their alkali metal salts, and hydroxides react with (HF).
   C) Oxides are insoluble or give insoluble fluorides.
   D) Dichromates, chlorates, and permanganates react with (HF).

II. Conductivity of inorganic compounds in (HF).
   A) Water in (HF). $\Lambda_0 = 260$ $\alpha(.5N) = 46\%$
      1. H_2O may dissociate into H^+ and OH^- or into H_3O^+ and F^-.
      2. If former, $H_2O + KF = K^+ + OH^- + (HF)$; then conductivity of H_2O and KF together should equal that of KF alone.
      3. Results show that reaction is: $(H_3O^+F^-) + (K^+F^-) = H_3O^+ + K^+ + 2F^-$.
         a. Then conductivity equals sum of conductivities of KF alone and H_2O alone.
         b. Concentration cell results indicate increase of fluoride ion concentration when H_2O is added to (HF).
   B) KNO_3 in (HF). $\Lambda_0 = 625$.
      1. Conductivity is very high - twice that of KF.
      2. Reaction is: $KNO_3 + 2HF = H_2NO_3^+ + K^+ + 2F^-$.
   C) Other conductivity work shows similar reactions.
      1. $HAc + HF = H_2Ac^+ + F^-$.
      2. $KAc + 2HF = K^+ + H_2Ac^+ + 2F^-$.
      3. $HNO_3 + HF = H_2NO_3^+ + F^-$.
      4. $H_2SO_4 + HF = HSO_3F + H_2O$
      5. $K_2SO_4 + 2HF = KF + KSO_3F + H_2O$.

III. Raising of boiling point by above compounds confirms reactions.
   A) Rise due to KAc is equal to the sum of the rise due to HAc and rise due to KF.
   B) Rise due to KNO_3 is equal to the rise due to HNO_3 and the rise due to KF.

IV. Conclusions.
   A) Liquid hydrogen fluoride is an excellent electrolytic solvent.
   B) The only anion that seems capable of existing in (HF) is the fluoride ion. Alkali metal halides, for example, react with (HF) to give the corresponding halogen acid. Many other salts form complex cations together with the fluoride ion when added to (HF). In no case has there been found any anion in (HF) solution except the fluoride ion.

References:

Karl
Fredenhagen and Gustav Cadenbach; Z. physical Chem. 146, 245, (1930).
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Bond and Stowe; J. Am. Chem. Soc. 53, 30, (1931).
Fredenhagen, Cadenbach and Willi Klatt; Z. physical Chem. 164, 176, (1933).

Inorganic Seminar November 24, 1936

SOME RECENT WORK ON THE NITRIDES OF PHOSPHORUS

1. General methods for the preparation

2. PN
   (a) Reaction of PCl_3 with NH_3. The reaction proceeds in accordance with the diagrammatic scheme.

$$PCl_3 + 6NH_3 \xrightarrow{-70^\circ} P(NH_2)_3 + 3NH_4Cl$$

$$P(NH_2)_3 \xrightarrow{80^\circ} PNH.NH_2 + NH_3$$

$$2PN.NH_2 \longrightarrow P_2(NH_2)_3 + NH_3$$

$$3P_2(NH_2)_3 \xrightarrow[\text{to } 560\text{-}600^\circ]{\text{heated in vacuum}} P_4N_6(?) \xrightarrow{750^\circ} PN + N_2 \xrightarrow{1000^\circ} (PN)_n$$

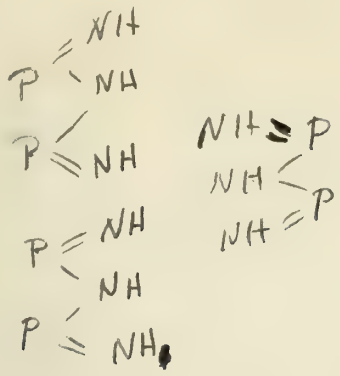
   (b) Properties of P_4N_6
   (c) Properties of PN

3. P_3N_5
   (a) Reaction of $P_3N_3Cl_6$ with NH_3-
   (b) Reaction of PCl_5 with NH_3
   (c) Properties of P_3N_5 -

4. References

   (a) Renaud, P.
       Bull. soc. chim. 53 , 692-7 (1933)
   (b) Mouren and Rocquet
       Compt. rend. 197, 1643-5 (1933)
   (c) Mouren and de Ficquelmont
       Compt. rend. 198, 1417-19 (1934)
   (d) Mouren and Rocquet
       Compt. rend. 198, 1691-3 (1934)
   (e) Mouren and Wetroff
       Compt. rend. 201, 1381-3 (1935)

J. Kleinberg



THE FLUOROCHLOROSILANES

November 24, 1936

I. Historically, of the silicon derivatives, SiF_4 and $SiCl_4$ were known long before silane, SiH_4, while
   A) Mixed fluorine halides of carbon were prepared by Swarts in 1892 by the use of the reaction

$$CHCl_3 + SbF_3 \cdot Br_2 \longrightarrow CHCl_2F + SbF_2Cl \cdot Br_2$$

   B) Rule of Swarts
   C) Schumb and Gamble prepared SiF_3Cl and SiF_2Cl_2 by exploding hexafluorodisilane with chlorine.
   D) Booth generalized the Swarts reaction for Group III and IV compounds, using SbF_3 with $SbCl_5$ as the catalyst first for the preparation of derivatives of some carbon compounds.

II. The preparation of the fluorochlorosilanes included apparatus more or less specialized.
   A) A catalyst is necessary for fluorination; pentavalent antimony is better than free halogen
   B) Of the three methods tried for stepwise fluorination, the best was the slow addition of the catalyst to a vigorously stirred mixture of SbF_3 and $SiCl_4$.
   C) Analysis of the fractions and molecular weight determinations proved the isolation of the series $SiCl_3F$, $SiCl_2F_2$, and $SiClF_3$.

III. Melting and boiling points show a deviation from the Swarts' Rule.
   The critical constants and the vapor pressures were measured.

IV. Two mechanisms are used to explain the different reactions,
   A) Non-polar halides which are covalently unsaturated

$$SiCl_4 + SbCl_2F_3 \longrightarrow Cl_4Si\begin{matrix}\swarrow F\\ \nwarrow F\end{matrix}SbFcl_2 \longrightarrow SiFCl_3 + SbF_2Cl_3.$$

   B) Non-polar halides which are covalently saturated

$$CCl_4 + SbF_3Cl_2 \longrightarrow Cl_2C\begin{matrix}\swarrow Cl\\ \nwarrow Cl\end{matrix}SbFSCl_2 \longrightarrow CFCl_3 + SbF_2Cl_3$$

References: Booth and Swinehart, J. Am. Chem. Soc. 57, 1333-42 (1935)
Schumb and Gamble, J. Am. Chem. Soc. 54, 3943-9 (1932).

A. G. Sharp

Inorganic Seminar

December , 1936

Deuterium as an Indicator of the Course of Chemical Reactions

W. A. Taebel

I. History

II. Detection and Estimation
1. Spectrum analysis
2. Mass spectrograph
3. Density methods
   a-Pycnometer
   b-buoyancy balance
4. Refractive index

III. Methods of concentration
1. Distillation
2. Electrolysis
3. Diffusion
4. Absorption

IV. Factors influencing chemical properties
1. Mass
2. Zero-point energy
3. "Tunnel" passage of potential barrier

V. Use in the field of Biochemistry
1. Study of metabolism
2. Identification of intermediate compounds

VI. The reversibility of the photodecomposition of ammonia

VII. Possible mechanisms of catalytic hydrogenation
1. Addition and detachment occur simultaneously
2. Detachment follows the addition at some interval

VIII. Facts supporting mechanism No. 2
1. Importance of the double bond
2. Cis-trans inversion
3. Wandering of double bond
4. Less energy of activation

IX. Complete mechanism of hydrogenation
1. The active adsorption of the hydrogen as atomic hydrogen
2. The active adsorption of the unsaturated compound with the resulting opening of the double bond.
3. Transfer of hydrogen atom to one of the carbon atoms thus forming the half-hydrogenated state. This may be followed by
4. a) Elimination of hydrogen atom
   b) Subsequent attachment of hydrogen to another carbon atom.

X. Keto-enol tautomerism of acetone
1. The use of deuterium oxide adds more evidence to the view that acetone is a tautomer.

XI. Neutralization of the pseudeo acid nitroethane

Ref. James, T. H.; J. Chem. Ed. 13, 458-62 (1936)

Inorganic Seminar December 15, 1936

ARTIFICIAL RADIOACTIVITY

I. Historical
   a) Curie and Joliot's original work
   b) Use of neutrons by Fermi

II. Eight types of reactions which produce artificial radioactivity

III. Identification of radioactive isotopes by electrical methods.

IV. Concentration of radioactive elements
   a) Chemical reactions
   b) Electrochemical deposition
   c) Dissociation methods
   d) Physical methods

V. Use of slow neutrons in the production of artificial radioactivity
   a) Production of slow neutrons
   b) Reactions of slow neutrons
   c) Velocity selector for slow neutrons

VI. Specific examples of production of Radioactive elements.

Ridenour and Yost Chem. Rev. 18, 457 (1936)

G. E. Babcock

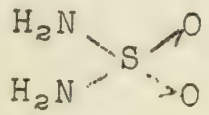
INORGANIC SEMINAR.

December 22, 1936

SULFAMIDE

I. Historical survey--Sulfamide was first prepared by Reynard in 1838.
Investigations now being carried out by F. G. Mann and F. G. Wood.

II. Properties and structure of sulfamide
1. Sulfamide is a white crystalline substance melting at 93°.
2. Chemical properties quite analogous to urea--as might be expected from structural similarities.
3. Recent parachor measurements assign this structure to sulfamide.



III. Methods of preparation.
1. Addition of dilute aqueous ammonia to sulfuryl fluoride.
2. " " sulfuryl chloride to a solution of ammonia in ethyl acetate.
3. Ammonia (gas) passed into a solution of ammonia in ethyl acetate.
4. Sulfuryl chloride added to a solution of sodamide in ligroin
5. " " " " liquid ammonia.

IV. Condensation reactions between sulfamide and formaldehyde.
1. Sulfamide and ammonia condense to form water clear resins.
2. Analyses of the resins formed and formulae suggested.
3. Condensations of derivatives of sulfamide and formaldehyde
   a) Unsymmetrical dimethyl-sulfamide
   b) Aniline p-sulfonamide

V. Reaction between sulfamide and xanthydrol

VI. Preparation of some complex metallic salts of sulfamide
1. Sodium di-aquo rhodium disulfamide
2. " mono-ammino mono-hydroxy platinic disulfamide

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Franklin, E. C. "The Nitrogen System of Compounds" Rheinhold Publ. Co. (1935)

Sister M. Josetta

Inorganic Seminar

January 4, 1937

RHENIUM HALIDES

I. Rhenium fluorides

A. Ruff and Kwasnik among others, Z. allgem. 125, 226 obtained pale yellow ReF_6, melting at 18.8°C. and boiling at 47.6°C., by passing dry, pure F_2 over powdered Re, using quartz apparatus. ReF_6 etches glass and quartz; it reacts with Na, Ca, and metallic oxides. On oxidation or reaction with quartz or glass it gives colorless $ReOF_4$. Reduction with CO, H_2, or SO_2 gives ReF_4.

B. Ruff and Kwasnik obtained micro-crystalline or amorphous dark green ReF_4, melting at 124.5°C., by treating Re powder with pure, dry F_2 under diminished pressure; or by the reduction of ReF_6. At 250° it is reduced by H_2 to the metal; at 100° with H_2S it gives a rhenium sulfide; at 500° in air it forms oxy-fluorides. With KF in H_2F_2 solution it gives K_2ReF_6. ReF_4 etches glass and quartz; it reacts with water, forming H_2F_2 and a black-brown ppt.

C. According to Ruff and Kwasnik ReF_7 cannot be formed because the ionic radius of Re^7 is too small (less than .55 A.u.) to permit 7 fluorine ions (ionic radius = 1.33 A.u.) being grouped around it. All attempts to prepare it have failed.

II. Rhenium chlorides

A. Dark colored $ReCl_5$ is formed by passing Cl_2 over Re at 500°. Repeated sublimation in vacua purifies the product. The thermal decomposition of $ReCl_5$ in a stream of N_2 gives $ReCl_3$ and Cl_2. Oxidation of $ReCl_5$ is represented by the equation: $8ReCl_5 + 7O_2 \longrightarrow 5ReOCl_4 + 3ReO_3Cl + 17Cl$. Dry KCl and $ReCl_5$ yield yellow-green crystals of K_2ReCl_6, slightly soluble in H_2O. $ReCl_5$ with 10% NaOH precipitates hydrated ReO_2 and forms in solution $NaReO_4$. With H_2O $ReCl_5$ reacts vigorously, producing hydrated ReO_2, $HReO_4$, Cl_2, HCl, and rhenium oxychlorides. Reduction with hydrogen gives metallic Re and HCl. Klemm and Frischmuth report the formation of ammoniates of $ReCl_5$ at liquid NH_3 temperatures. $ReCl_5$ ammonolyzes even at room temperature.

B. Dark red crystals of $ReCl_3$ can be obtained by treating the liquid fractions obtained from the chlorination of Re with metallic Re at 500°. $ReCl_3$ is also formed by the thermal decomposition of Ag_2ReCl_6: $2Ag_2ReCl_6 \longrightarrow 4AgCl + ReCl_3 + ReCl_5$. $ReCl_3$ can be purified by taking advantage of its varying solubility in HCl-(gas)-saturated ether and aqueous HCl of varying concentrations. $ReCl_3$ reacts with H_2O to form Re_2O_3. In acid solution this hydrolysis is checked, 13% HCl (or greater concentrations) being the most efficient. Ammonia and NaOH solutions cause the formation of ReO_4^-, Re^4, Re^2. $ReCl_3$ in acid solution is ~~very~~ fairly stable to oxidizing and reducing agents; solid $ReCl_3$ on heating in air gives oxychlorides; Zn and nascent H reduce Re^3 to Re^1 at 5°. $ReCl_3$ reacts slowly with H_2S; gives no reaction with solutions of KCl, RbCl, or CsCl; is reduced at 240-300° with H_2 to the metal and HCl. Several ammoniates of $ReCl_3$ have been prepared in different ways. At temperatures of 100° or above $ReCl_3$ ammonolyzes. Geilmann and Wrigge report that $ReCl_3$ is not a true salt since it gives no reaction with $AgNO_3$.

$ReCl_3 \cdot 6NH_3$ $ReCl_3 \cdot 7NH_3$

$ReCl_3 \cdot 14NH_3$

C. Solid $ReCl_2$ apparently has not been isolated, but Re^2 has been detected in chloride solution. Decomposition of K_2ReCl_6 by NaOH solution takes place according to the valence equation: $9Re^4 \longrightarrow 3Re^2 + 4Re^4 + 2Re^7$. After removal of Re^4, Re^7 and Re^3 (formed as an intermediate), the solution required 2.49 mols of oxygen to change one mol of the Re in solution to Re^7, indicating that Re^2 was present in the solution. The solution has strong reducing properties; on oxidation it gives Re^7. H_2S produces a black ppt.

D. ReCl is produced by the reduction of an ice-cold, strongly acid solution of $ReCl_3$ with Zn or Na amalgam. Oxidation of the solution with K_2CrO_4 shows that 1 mol of the Re in solution requires 3 mols of oxygen to give 1 mol of Re^7; therefore Re^1 is in solution. The solution has very strong reducing properties, reducing indigo sulfonate in the cold. Other properties are as yet little investigated.

E. $ReCl_7$: Noddack reported the preparation of green, crystalline $ReCl_7$ by passing Cl_2 over gently heated Re. $ReCl_7$, according to Noddack, hydrolyzes to give ReO_4^- and a black ppt. of unknown composition. Briscoe and co-workers report that under those conditions no green crystals are obtained. Geilmann and co-workers write that brownish-black $ReCl_5$ is formed under those conditions. Hagge and Kwasnik state that $ReCl_7$ cannot be formed due to the size of Re^7 and Cl^1.

F. Noddack reported brown, liquid $ReCl_6$, but later wrote that the brown liquid is $ReOCl_4$.

G. $ReCl_4$: Briscoe and co-workers report the formation of black, crystalline $ReCl_4$ on passing Cl_2 over Re at 250° (about the conditions under which Noddack claims to have prepared $ReCl_7$). Geilmann says that Briscoe's product is a mixture of chlorides, and that chiefly brown-black $ReCl_5$ is formed. From vapor density measurements Yost and Shull find that: $2ReCl_4(g) \longrightarrow Re_2Cl_8$. They obtain $ReCl_4$ as black or dark red crystals.

III. Rhenium bromides: the only rhenium bromide that has been prepared to date is blackish, crystalline $ReBr_3$, which was prepared by passing Br_2 vapor at a reduced pressure over rhenium at 450-600°. Resublimation in a N_2 atmosphere purifies the product. Distillation in air gives a blue product, probably one or more oxybromides, which have not as yet been isolated; therefore their analysis and study has not been possible. Schüth and Klumm prepared considerable quantities of $ReBr_3$ by thermal decomposition of a double silver-rhenium bromide. $ReBr_3$ forms ammoniate with liquid NH_3.

IV. Rhenium iodides: W. Noddack reports that with I_2 vapor Re forms a dark liquid compound "which has not as yet been investigated further."

Charles Harmison

I and ~~Amyl~~

References

1. W. Noddack Zeit fur Anorg. and All Chem. 215, 149 (1933)
2. Hagen and Sieverts " " 215, 111 (1933); 219, 65 (1934)
3. W. Geilmann, F. Wrigge, and W. Biltz " 214, 344 (1933)
4. W. Geilmann and F. Wrigge " 214, 248 (1933)
5. F. Wrigge and W. Biltz " 228, 372 (1936)
6. W. Klemm and G. Frischmuth " 230, 209 (1937)
7. Briscoe and co-workers Jour. Chem. Soc, (London) 1931, II, 2263
8. Yost and Shull Jour. Am. Chem. Soc, 54, 4657 (1932)

Inorganic Seminar

January 13, 1937

THE ABUNDANCE OF RARE EARTHS IN METEORITES.

I. Sources of Meteorites Analysed

II. General Composition of Stony and Metallic Meterorites

III. Preparation of Material for Analysis
   1. Mechanical scraping and grinding
   2. Chemical preparation of concentrate containing the rare earths
      a) Methods for removal of other elements
      b) Precipitation of rare earths
   3. Control experiment for determination of completeness of separation

IV. Preliminary treatment before X-ray Analysis
   1. Regulation of degree of oxidation
   2. Preparation of artificial control mixtures

V. X-ray Analysis of Concentrates
   1. Conditions for X-ray spectroscopy
   2. Internal standard
   3. Selection of lines
   4. Photometry of lines and calculation of percentages

VI. Concentration of rare earths in meteorites

VII. Comparison with concentration of rare earths in earths crust

Margaret Lawrenz

Ref. The Abundance of the Rare Earths in Meteorites by Ida Noddock
Zeitschrift für Anorganische und Allgemeine Chemie 225 337-364 (1935)

INORGANIC SEMINAR February 16, 1937

NEW ALLOYS AND THEIR USE IN CHEMICAL INDUSTRIES

I. Problems confronting metallurgists
   1. Temperature
   2. Motion, vibration and torsion
   3. Corrosion
      a. atmospheric
      b. chemical

II. Developments in ferrous alloys
   1. Improvements in stainless steel
   2. Low alloy steels

III. Non-ferrous alloys
   1. Cr, Ni alloys (Monel-K)
   2. Pb, Sn, Zn + Sb alloys
      a. Gun spraying
   3. Cu alloys
      a. Cu - Be
         1) Physical properties
         2) Uses
         3) Future

IV. References: Symposi~~tion~~um, Inds. Eng. Chem. 28,1366-1424 (1936)

J. P. McReynolds

ALKALI SALTS OF THE BORON HYDRIDES AND THEIR IMPLICATIONS TO THE STRUCTURE OF THE HYDRIDES.

Inorganic Seminar

February 23, 1937

I. Theories on the structure of the boron hydrides
   a. Former hypotheses
   b. Wiberg's ethylenic structure theory. Evidence for this theory
   c. Significance of the alkali salts to the substantiation of Wiberg's structure

II. Alkali salts of diborane.
   a. $K_2(B_2H_6)$. Preparation:
      1. Preparation of B_2H_6 by decomposition of B_4H_{10}
      2. Reaction between potassium amalgam and diborane mechanism. Apparatus used.
   b. Chemical properties of $K_2(B_2H_6)$
      1. Sublimes at 400° with partial decompsotion into hydrogen, potassium and solid $K_2B_4H_4$
      2. Reaction with halogen acids. Two possible reactions:

$$K_2(B_2H_6) + 2HBr \longrightarrow 2KBr + B_2H_6 + H_2$$
$$K_2(B_2H_6) + 4HBr \longrightarrow K_2(B_2B_4H_2) + 4H_2$$

      3. Hydrolysis: goes in steps.

$$1)\ K_2(B_2H_6) + 2H_2O \longrightarrow K_2(B_2H_4(OH)_2$$
$$2)\ K_2(B_2H_6) + 6H_2O \longrightarrow K_2[B_2(OH)_6] + 6H_2 \longrightarrow K_2[B_2(OH)_2O_2]$$
$$3)\ K_2(B_2H_6 + 4H_2O \longrightarrow 2KBO_2 + 7H_2$$

      Mechanism of the hydrolysis according to the Wiberg Hypothesis

III. Potassium salts of B_4H_{10} and B_5H_9
   a. $K_2(B_4H_{10})$
      1. Preparation of the tetraborane. Action of phosphoric acid on magnesium boride. Purification by fractional condensation.
      2. The reaction between B_4H_{10} and potassium amalgam.
      3. Thermal decomposition of $K_2(B_4H_{10})$.

IV. Potassium salt of B_5H_9

V. Other salts of the boron hydrides which have recently been prepared.

References:
Wiberg Ber 69B 2816-39 (1936)
Stock, Sutterlin, and Kurzen: Z. anorg. allgem. Chem. 225, 225-242
Stock, Kurzen, and Laudenklos: " " " " 225, 243-253
Wiberg; " " " " 225, 262-269
Stock and Laudenklos: " " " " 228, 178-192

Harry H. Sisler

Inorganic Seminar

March 9, 1937

LIQUID AND SOLID HYDRIDES OF PHOSPHOROUS

I. Preparation of diphosphine, determination of the molecular weight and other physical constants. Absence of higher homologues. Non existance of salts such as $P_2H_4.HCl$ analogous to $N_2H_4.HCl$.

II. Decomposition of diphosphine to give the solid hydride of phosphorous. Royan's theory that the solid hydride is an adsoprtion compound of PH_3 on yellow amorphous phosphorous.

$$3P_2H_4 = 4PH_3 + 2P$$

Evidence from Debye-Scherrer x-ray patterns and thermal decomposition of the solid hydride to yield PH_3.

III. Stock's hydride P_9H_2 - Evidence favoring the view this is not a definite hydride but an adsorption product. Comparison of solubilities in CS_2 and melting points with the definite polyhydrides of sulphur indicates that P_9H_2 has probably no sulphur analog. Acidic properties are absent.

IV. The solid hydride of phosphorous and its apparent acidic properties. Compounds with piperidine and ammonia. Evidence that these are adsorption products.

V. Preparation of yellow amorphous phosphorous and adsorption of triethyl phosphine. Synthesis of a solid hydride from the components Pond PH_3. Comparison with other preparations.

VI. Attempts to prepare halogenated phosphines.
a) Treatment of PH_3 with Br_2, PBr_3 Or PCl_5
b) Stock's reaction with halogen acids in presence of $AlCl_3$.
Attempts to prepare substituted halogenated phosphines.
Condensation of diphenyl chlorophosphine with PH_3 to give an adsorption compound.

References: P. Royan and K. Hill - Johann Wolfgang Goethe Univ. Frankfort A. M.
Zeit. anorg u. allgem. Chem. 229 97 (1936)
229 112 (1936)
229 369 (1936)

W. J. Peppel

Reduction of SO_2 by C. → S.

Angew. Chem. 49, 540 (1936)

Dr E. Guenther Fritzsche Bros, Inc
118 W Ohio St
Chicago

INORGANIC SEMINAR

March 16, 1937

Jacob Kleinberg

"CHEMISTRY IN LIQUID SO_2"

Jander and Wickert

Z. physik, Chem. (A) 178, 57-73 (1936)

I. Introduction

$$2H_2O \rightleftharpoons OH^- + (H.H_2O)^+ \rightleftharpoons (OH^-) + (H_3O)^+$$

$$2NH_3 \rightleftharpoons (NH_2)^- + (H.NH_3)^+ \rightleftharpoons (NH_2^-) + NH_4^+$$

$$2SO_2 \rightleftharpoons (O.SO_2^{--}) + (SO)^{++} \rightleftharpoons (SO_3^{--}) + (SO)^{++}$$

II. Previous observations $SO_2 \rightleftharpoons (SO)^{++} + (O^{=}) \rightleftharpoons S^{++++} + 2O^{=}$

III. Data on the solubility and conductivity of substances in liquid SO_2

IV. Neutralization reactions in SO_2 $K_2SO_3 + SOCl_2 \rightarrow KCl + SO_2$
(According to the researches of Heinz Immig)

V. Reactions with the participation of the solvent, SO_2

VI. Further reactions in liq. SO_2

$$K_2SO_3 + OS(OC_2H_5)_2 \rightleftharpoons KOC_2H_5 + 2SO_2$$

$$2[(C_2H_5)_3N \cdot SO_2] + KBr \rightarrow \left[\begin{matrix}(C_2H_5)_3N \\ O=S \\ (C_2H_5)_3N\end{matrix}\right]Br_2 + K_2SO_3$$

$$\therefore \left[\begin{matrix}(C_2H_5)_3N \\ (C_2H_5)_3N\end{matrix}>SO\right]SO_3$$

cond. $2[(CH_3)_4N]_2SO_3 + OS(OC_2H_5)_2 \rightarrow 2(CH_3)_4NOC_2H_5 + 2SO_2$

$2HI + O(C_6H_4)O \xrightarrow{SO_2} HO(C_6H_4)OH + I_2$

$M_2SO_3 \cdot SO_2 \rightarrow M_2S_2O_5$.

$PCl_3 + H_2O \rightarrow H_3PO_3 \xrightarrow[\text{Retention}]{\text{Dum.}} H_3PO_4$

(oxidizing, free I_2

Dum. $\rightarrow$ $P(OH)_3 \xrightarrow{\text{Spalting}} HP(OH)_2O$

Splitting off with Formed.

Inorganic Seminar

March 30, 1937

CERTAIN ASPECTS OF THE MODERN THEORIES OF CORROSION

I. Historical

II. Theories of Corrosion
   1. The Acid Theory
   2. The Hydrogen Peroxide Theory
   3. The Electrochemical Theory

III. Types of Corrosion affecting immersed metals
   1. Hydrogen - evolution type
   2. Oxygen - diffusion type

IV. Mechanism of Atmospheric corrosion

V. Factors affecting the velocity of corrosion

VI. The distribution of corrosion

VII. Prevention of Corrosion

1. Mayne, J.E.O., J. Chem. Soc. 366 (1936)
2. Ibid 1095 (1936)
3. Evans, U. R. The Corrosion of Metals. E. Arnold and Company. London 19~~36~~ -26

W. A. Taebel

Inorganic Seminar

April 6, 1937

TAUTOMERISM OF SOME BRIDGED DI-PALLADIUM DERIVATIVES

I. Coördinate links

II. Preparation and properties of palladous derivatives of the types:

$[(R_3P)_2PdCl_2]$ $[(R_3As)_2PdCl_2]$ $[(R_2S)_2PdCl_2]$

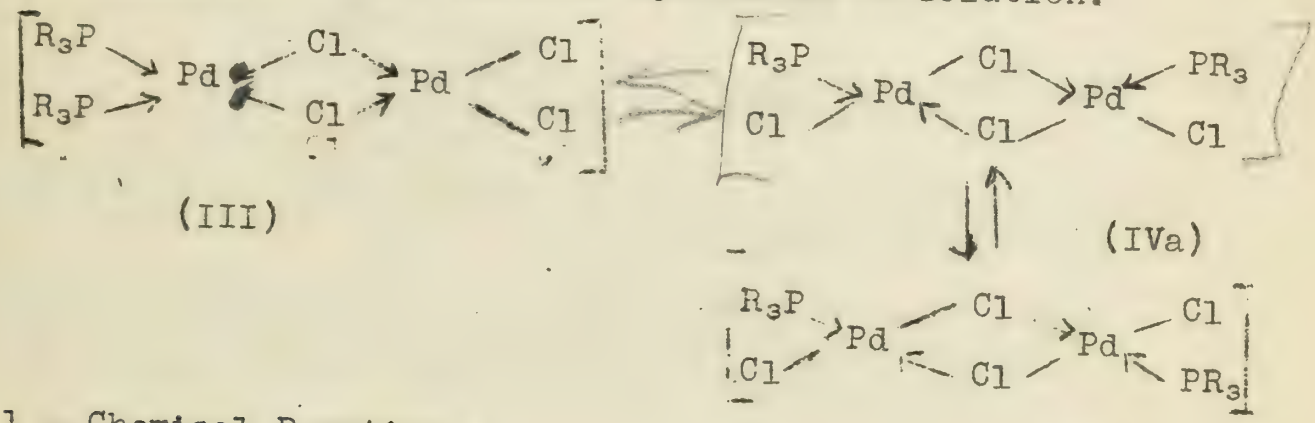
III. Preparation of bridged di-palladium derivaties from the di(phosphine, arsine or sulfide) dichloro palladium complexes.

1 - $[(R_3P)_2PdCl_2] + (NH_4)_2PdCl_4 = [R_3PPdCl_2]_2 + 2nH_4Cl$

2 - $[(R_3As)_2PdCl_2] + \Delta = [R_3AsPdCl_2]_2 + 2R_3As$

3 - Properties and structure of the new series of compounds

IV. Evidence for the following equilbrium in solution:



1 - Chemical Reactions

2 - Dipole moment measurements

V. Significance of results in regard to structure of some previously reported compounds

1 - Pt and Pd compounds in which the metal apparently has coordination number of five.

2 - Wolffram's red salt

VI. Anomalous Parachor of Palladium

Mann and Purdie Journal of theCChemical Society 1935 1549-1563; 1936 873-890

C. L. Rollinson

Inorganic Seminar April 13, 1937

RECENT DEVELOPMENTS IN THE UTILIZATION OF CADMIUM

I. Introduction.
   A. History of the utilization of Cadmium[1]
   B. Cadmium production
      1. Sources
      2. Quantities
   C. The market for Cadmium in the last few years

II. Utilization of Cadmium in bearing metal alloys.
   A. General requirements of bearing alloys.
      1. Former requirements.
      2. Present day demands on bearing metal alloys.[2]
   B. Are the ordinary babbitt metals, which have been satisfactory for years, capable of meeting these new demands?[3,4]
   C. Cadmium base bearing metal alloys as a solution for this problem.[5,6]
      1. Cd-Ag-Cu alloys[3,6,7,8,9]
         a. Composition, properties, and production
         b. Comparison with ordinary babbitts
      2. Cd-Ni alloys.[4,10]
         a. Composition, properties, and production
         b. Comparison with ordinary babbitts.
      3. Cd-Co; Cd-Mg-Cu.[1,5]
   D. Cd as a minor addition to other bearing metal alloys.
   E. Prospect of Cadmium in the bearing metal industry.[5]

III. Other alloys containing cadmium; their properties and uses.
   A. Use of Cd and Cd alloys as corrosion resistors.
   B. Miscellaneous other alloys containing cadmium.

References:

1. Mineral Industry, 44, 631-4. (1935)
2. Rabinovitch, T., Petroleum Z. No. 41, Motorenbetrieb u. Maschinenschmierung 8, No. 10, 2-5 (1935)
3. Business Week, Apr. 18, 1936. p. 36.
4. Metal Ind. 33, 142 (1935)
5. Gill, Alan S., Proc. Australasian Inst. Min. Met., 95, 201-7 (1934)
6. Phillips, A. J., Prod. Eng. 6, 365 (1935)
7. Denham, Athel F., Automotive Ind., 71, 640-42
8. Blomstrom, L. C., Prod. Eng. 6, 364 (1935)
9. Steel, 96, 34 (1935)
10. Aero Digest, 26, 50 (1935)

INORGANIC SEMINAR - April 30, 1937

"REACTIONS OF IRON AND NICKEL WITH HYDROGEN CHLORIDE IN VARIOUS SOLVENTS"

I. The reaction of HCl dissolved in the following organic liquids on metallic Fe and Ni fall into three groups.

I	II	III
H_2O	$(C_2H_5)_2O$	$CHCl_3$ (Ni)
CH_3OH	CH_3COOCH_3	CCl_4
C_2H_5OH	$CH_3COOC_2H_5$	CS_2
$n\text{-}C_3H_7OH$	$CHCl_3$ (Fe)	C_6H_6
$iso\text{-}C_3H_7OH$		$C_6H_5NO_2$
CH_3COOH		light petroleum

Group I. Both metals attacked rapidly with evolution of heat.
Group II. Reaction much slower with no appreciable evolution of heat. Coordination compounds formed.
Group III. No reaction on either metal.

II. The liquids in Group I showed an increase in conductivity when saturated with HCl, showing that the reaction is probably ionic. Group II liquids show practically no change in conductivity after saturation with HCl, and therefore the reaction is probably molecular.

III. Except in cases of liquids with similar structure, there was no connection between the dielectric constant and the extent of ionization. For example, K for $C_6H_5NO_2$ is 36.1, and yet negligible ionization takes place. The K for n-propyl alcohol is 13.3 and yet there is a great deal of ionization.

IV. Under the same experimental conditions, $FeCl_2$ coordinates twice as many solvent molecules as does $NiCl_2$ in nearly every case.

$NiCl_2 \cdot CH_3OH$	$NiCl_2 \cdot 2CH_3OH$
$FeCl_2 \cdot 2CH_3OH$	$FeCl_2 \cdot 4CH_3OH$
$2NiCl_2 \cdot CH_3COOCH_3$	$2NiCl_2 \cdot C_3H_7OH$ (iso)
$FeCl_2 \cdot CH_3COOCH_3$	$FeCl_2 \cdot C_3H_7OH$ (iso)

exception $NiCl_2 \cdot C_2H_5OH$
$FeCl_2 \cdot C_2H_5OH$

References: D. R. Chesterton, "Complex Iron Compounds Part I. The Formation Solvation of Ferrous Chloride in Non-Aqueous Liquids." J. Chem. Soc. Part 2, 906-910 (1935)

D. R. Chesterton and A. S. Nickelson, "Complex nickelous compounds. Part I. The Formation and Solvation of Nickelous chloride in some Non-aqueous Liquids." J. Chem. Soc. 1300-1302(1936)

Both authors at Woolwich Polytechnic, London

M. Sveda

Inorganic Seminar - April 20,1937

THE CHLOROFORM CHLORINATES

I. Introduction
   1. Some aspects of molecular compounds

II. Experimental procedure

III. Data

IV. Findings - Existence of the following chloroform chlorinates
   1. Chloroform hemichlorinate $(CHCl_3)_2 \cdot Cl_2$
   2. Chloroform monochlorinate $CHCl_3 \cdot Cl_2$
   3. Chloroform dichlorinate $CHCl_3 \cdot 2Cl_2$
   4. " trichlorinate $CHCl_3 \cdot 3Cl_2$

References

Pfeiffer Organische Molekülverbindungen
Wheat and Brown J.A.C.S. 58, 2410 (1936)

V. F. Balaty

INORGANIC SEMINAR April 27, 1937

THE IDENTITY OF FERMI'S REACTION OF ELEMENT 93 WITH ELEMENT 91

I. INTRODUCTION

A. Fermi's Experiments
Neutron bombardment of uranium to produce an artificial radioactive element (No. 93). Its identification by its chemical properties.

B. Grosse and Argruss' Work
Repetition of Fermi's chemical experiments using proactinium (longest lived isotope of element 91) an indicator instead of element 93.

II. MATERIALS AND PROCEDURE

A. Materials
Materials used in repeating Fermi's chemical experiments proactinium, manganese dioxide, potassium perrhenate.

B. Procedure
1. Manganese dioxide as carrier
Precipitation of proactinium with manganese dioxide.
2. Rhenium sulfide as carrier
Precipitation of proactinium with rhenium sulfide.

III. PROPERTIES OF EKARHENIUM (93) AND EKAOSMIUM (94)

A. First Possibility
Electron distribution according to the periodic law and prediction of properties.

B. Second Possibility
Properties according to Bohr's theory of electron distribution

IV. DISCUSSION OF RESULTS AND CONCLUSIONS

A. Evidence proving that element 93 is an isotope of element 91.

B. Evidence which is contradictory

References: J.Amer.Chem.Soc. 57, 438-440 (1935)
Nature 133, 757, 898 (1934)

Emil F. Frech

INORGANIC SEMINAR - April 27, 1937

ELEMENTARY FLUORINE

I. Introduction.

A. History of development.

Early work in field between 15th and 19th centuries. Prepared by Moissan in 1886. Method of preparation. Later improvements both on electrolyte and type of cell since 1900. Description of common type of cell now in use. Various metals which can be used in working with gaseous F_2.

II. General Characteristics of gaseous Fluorine.

Test for. - Spectroscopic picture of the atom - Ionization potential - Physical properties such as color, etc.

III. Reactions.

A. General
   Reactive materials
   Non-reactive materials

B. Specific as compared to anodic reactions. Very high oxidizing potential. Fichter and coworkers obtained persulfates, cobaltic salts, ozonates, perphosphates, etc. Best conditions for oxidations. Attempts to explain oxidations. Difficulties due to formation of H_2O_2 from H_2O.

C. Formation of unusual products. CCl_2F_2; AgF(gaseous F_2 on Ag salts yield Ag_2O_2); OsF_8; Ruff's work on halogen fluorides; F_2O; NF_3.

IV. Conclusions

Difficulties in working with gaseous fluorine
Possibility of commercial value

Bibliography

Jones, N. Jour. Phys. Chem. 33 801

Fichter Helv. Chim Acta 14 862 (1931)

Yost, D.M. and Hatcher J.B. - Hourn. Chem. Ed. 10 330(1933)

L. Whyte

Inorganic Seminar May 4, 1937

THE TELLURIUM ELECTRODE

Metal-metal oxide electrodes as substitutes for hydrogen electrode in pH measurements and acidimetric titrations.

I. Theoretical Considerations - slightly soluble metal oxide required, less active than hydrogen. One pH unit = .059 volts.

II. Metal - metal oxide electrodes
1. Early electrode systems
2. Sb, pH range metal-oxide 2-7 metal-sulfide 2-10 accuracy 0.05 pH, excellent for titrations.
3. Ge, potential not reproducible satisfactory for titrations.

III. The Tellurium Electrode
1. Preparation
   a. treatment of surface
   b. single crystals
2. Electrode Reactions
   a. Acidic pH < 9 $H_2TeO_3 + 4H^+ = Te^{+4} + 3H_2O$
   b. basic pH < 9 $TeO_3^{=} + 6H^+ = Te^{+4} + 3H_2O$
3. Applications
   a. range pH 0-12
   b. in presence of oxidizing agents HNO_3, $KMnO_4$
   c. " " " organic anions
   d. non-aqueous solutions

Literature

Sb Parks and Beard, J.A.C.S. 54: 865 (1932)
Ball Schmidt and Bergstresser, Anal. Ed. 6:60 (1934)
Ge Nichols and Cooper, Anal. Ed. 7:350-55 (1935)
Te Getman, Tr. Am. Electrochem. Soc. 64: 201 (1933)
Tomicek and Poupe, Czechoslovak Chem. Communications VIII, 11 (1936) Pittsburgh meeting A.C.S. Sept. 10-1936.

V. R. Sullivan

INORGANIC SEMINAR May 4, 1937

CRYSTAL CHEMISTRY

I. Building the units of matter into crystals
   A. Six crystal systems
   B. Fourteen space lattices
   C. Thirty-two point groups
   D. Two hundred and thirty space groups

II. The first law of crystal chemistry

The structure of a crystal is determined by: - 1) the relative numbers, 2) the relative size, and 3) the polarization properties of its building stones, (atoms, ions, or groups of atoms). Atomic weight plays no part in the building of a crystal.

   A. Applications of the first law to metals
      1) The applications of the electron concentration rule to inter-metallic compounds
      2) The conditions necessary for solid solution
   B. Application of the first law to ionic, covalent, and molecular crystals
      1) Effect of ionic radii on lattice type (Coordination number)
      2) Effect of polarization properties

References:

C. W. Stillwell, J. Chem. Educ. 13, 415 (Sept. 1936)
" " , Ibid 13, 469, (Oct. 1936)
" " , " 13, 521, (Nov. 1936)
" " , " 13, 566, (Dec. 1936)
" " , " 14, 34, (Jan. 1937)
" " , " 14, 131, (March 1937)

Author is at Dennison Manufacturing Co., Framingham, Massachusetts. Instructor at U. of I. 1930-1932

Na4Pb9
4 1/8 22.13

Albert R. Hanke

Hume - Rothery Rule

INORGANIC SEMINAR May 11, 1937

ORGANIC REAGENTS IN INORGANIC ANALYSIS

I. History of the development of organic reagents in inorganic analysis.

II. Salt forming properties and inner complex compounds.
   A. Acid atomic groupings in the organic molecule which give rise to salt formation: (SO_3H)-, (SO_2H)-, (COOH)-, (OH)-, (SH)-, (NOH)=, and (NH)=.
   B. Conditions must be such in the organic molecule that a complex compound can be formed through the saturation of the secondary valences of the metal atom contained as a neutral part in the molecule.
   C. Definite atomic groupings and the reaction medium are of great importance in determining the specificity of organic reagents.
      1. Dimethyl glyoxime and other syndioximes.
      2. Benzoin oxime) Destinction between specific reagents
      3. salicyl aldoxime) and special reagents.
      4. Anthranilic and quinaldic acids
      5. 8-hydroxy quinoline.

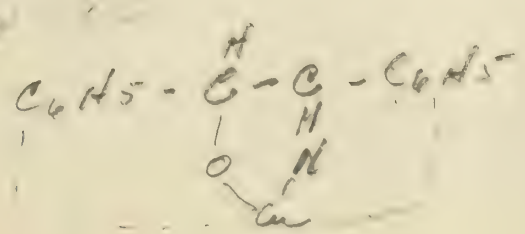
III. Specificity in normal salts.
   A. Organic compounds which are merely capable of forming normal heteropolar salts.
      1. phenylarsonic acid
      2. n-propyl arsonic acid
         (a). The - $AsO(OH)_2$ group alone is responsible for the activity of the organic derivatives of arsenic acid.
      3. Rhodanine for the detection of silver.
      4. Mercapto benzo thiazole for separation of Cu^{++} and Cd^{++}
      5. p-di-picryl amine for K^+

IV. Normal salt formation with organic cpds. plays an important role in the identification and estimation of anions.
   A. Nitron for gravimetric determination of perrhenate
   B. $(C_6H_5)_3SnCl$ for " " " fluoride

References

1. Organic reagents in inorganic analysis. Ind. and Eng. Chem. 28, 401, 409, 1936
2. Arnold, F. W. and Chandler, F. C., J.A.C.S. 57, 8 1935
3. H. H. Geist and G. C. Chandler, Ind. Eng. Chem. 9, 169, 1937

B. S. Marklein



INORGANIC SEMINAR

October 5, 1937

Anhydrous Sulfuric Acid as a Solvent

1. Unusual properties of pure anhydrous sulfuric acid. The pure liquid has a sufficiently high self ionization to give a concentration of 0.027 molar HSO_4 ions, a specific conductivity of 1×10^{-2} ohms^{-1} and a freezing point of 10.5c.

II. Technique and problems encountered in cryoscopic procedures with H_2SO_4 as solvent.

A. Preparation of the anhydrous solvent--add SO_3 to 95% acid to maximum freezing point. (SO_3 as 30% fuming acid).

B. Addition of enough water to complete the suppressing effect of the reaction $H_2O + H_2SO_4 \rightarrow H_3O + HSO_4$ upon the self-ionization of the acid.

III. Classes of compounds in the H_2SO_4 solvent system.

A. Non-electrolytes--Cl_3CCOOH; $(NO_2)_3C_6H_2OH$; $HClO_4$; $(CH_3)_2SOA$

B. Bases--H_2O; ROH; RCOR'; RCHO; RCOOH; ROR'; and all bases of the Bronsted type in water. ($Cl_2CHCOOH + C_6H_5NO_2$ show partial ionization)

C. Hydroxide analogues--$NaHSO_4$; $KHSO_4$; $Ba(HSO_4)_2$; etc.

IV. Triphenyl Carbinol behavior--Cryoscopic and conductivity data indicate that there are 4 ions per molecule of solute, Mechanism offered is

$$(C_6H_5)_3COH + 2H_2SO_4 \rightarrow (C_6H_5)_3C + H_3O + 2HSO_4$$

V. Behavior of di and tri substituted benzoic acids--these compounds also give data indicating the formation of 4 ions per molecule of solute, Mechanism.

$RCOOH + 2H_2SO_4 \quad RCO + H_3O + 2HSO_4$. Evidence in support of this mechanism other than appearance of 4 ions per molecule is found in the reactions of solutions of this type of acid in H_2SO_4 solution.

References: Hammett and Deyrup, J. Am. Chem. Soc. 55, 1900-9 (1933). Columbia University
Hammett and Lowenheim, ibid 56, 2670-5 (1934).
Treffers and Hammett, ibid 59, 1708-12 (1937)

J. P. McReynolds

A STUDY OF THE DIRECT OXIDATION OF PLATINUM, AND THE PROPERTIES OF THE PURE OXIDES

Historical

In 1904 Lothar Woehler showed that of all the hydrated oxides previously reported, only those of PtO and PtO_2 existed.

He also found that platinum black would form a slight amount of an oxide by heating with oxygen under pressure, but did not investigate very thoroughly.

Preparation

The pure oxides cannot be formed by dehydration of the hydrated oxides, because the temperature required to drive off the last molecule of water is so high that only platinum remains.

They can be formed by heating platinum in various states of subdivision with oxygen under pressure.

The oxygen for these investigations was furnished as indicated by the following equation:

$$10\ KMnO_4 \xrightarrow{\Delta} 2K_2MnO_4 + 3K_2MnO_3 + 5MnO_2 + \frac{13}{2}\ O_2\ .$$

The pressure of the oxygen can be predetermined by the starting quantity of potassium permanganate, and the temperature to which it is heated.

Compact platinum in the form of a wire reacts with only a very small amount of oxygen, viz., 0.015% to 0.022% by weight after 3 or 4 days under 150 atm. at 450°.

Spongy platinum undergoes a maximum oxidation at 460° for one day under 150 kg./cm², and contains 6.84% by weight of oxygen. Pure PtO would correspond to 7.57%. oxygen.

Platinum black for 12 hours at 440 to 450° under 130 kg./cm² gives a material having 12.30% by weight oxygen. Pure PtO_2 would correspond to 14.08% oxygen.

Pure PtO_2 was obtained by treating the mixture from the spongy platinum oxidation with aqua regia. The latter dissolves the Pt and PtO, and leaves the PtO_2 intact.

Pure PtO was prepared by heating platinum black at 430° under 8.25 kg./cm.² The time required depends on the fineness of the starting material.

Stability toward heat:

$$2PtO_2 \longrightarrow 2PtO + O_2 \text{ at } 400°$$

$$2PtO \longrightarrow 2Pt + O_2 \text{ at } 560°$$

This indicates that the oxides are relatively stable towards heat.

Catalytic Action:

PtO_2 and PtO are much better catalysts for hydrogenation than is ordinary platinum black as shown by studies on α pinene and phenol.

Reference: Pierre Granddam, Ann. de Chim. [11] 4, 83-105 (1936)

October 12, 1937 Michael Sveda

INORGANIC SEMINAR October 19, 1937

Radon Hydrate

I. Historical: 1) Salts of Rare gases probably do not exist.
2) Coordination compounds of Xenon, Argon, and Krypton has been formed. These are formed with compounds having a dipole
3) Radon should form a hydrate more stable than those of Krypton and Zenon

II. Mass Law relations in the formation of gas hydrates.
1) The applicability of the mass law to the dissociation of a gas hydrate has been proven.
2) In the pressence of constant vapor pressure the mass law expression for a gas hydrate dissociation becomes

$$\frac{M.nH_2O}{M} = K \text{ from which we have}$$

$$\frac{M.nH_2O}{M + nH_2O} = \alpha = \text{const.}$$

III. The distribution of Rn between the gas phase and the solid crystalline $SO_2.6H_2O$ was studied and it was shown by the law of Bertholet - Nernst that due to the constancy of the partition constant:

$$D = \frac{\% \text{ Rn in cryst.}}{\% \text{ Rn in gas}} - \frac{\% SO_2 \text{ in gas}}{\% SO_2 \text{ in cryst.}}$$

Rn must form an hydrate isomorphous with $SO_2.6H_2O$
Exp. also carried out for $H_2S.6H_2O$ with positive results

Reference: Nikitin: Z. anorg. allgem. Chem. 227, 81-93 (1936)

Harry H. Sisler

Inorganic Seminar

October 26, 1937

pH PROPERTIES OF COLLOIDAL CARBON

1. Measurement of pH of colloidal carbons.

2. Factors affecting pH values.
   a) Uniformity of pH values through repeated water extraction.
   b) Retention of the same pH properties with organic solvent extraction.
   c) Effect of colloidal carbon on neutral salt solutions.
   d) Interrelation of pH, amount of volatile content, and adsorption index for diphenylguanidine.

3. Manner of accounting for the pH values and their variation.

4. Industrial implications of the pH findings.

References: Wm. B. Wiegland, Ind. and Eng. Chem., 29, 953-56 (1937).
Rhead and Wheeler, J. Chem. Soc., 103, 461(1913)

D. F. Peppard

Inorganic Seminar November 16, 1937

THE SALT-LIKE HYDRIDES

1. Introduction

2. Historical
   a) The work of Gay-Lussac and Thenard on Potassium Hydride
   b) Early conception of formulas of Hydrides
   c) Later work of Troost and Moissan on Lithium, Sodium and Potassium Hydrides
   d) Winkler and Hoffmeisters Work on Calcium Hydride

3. Classification of Hydrides
   a) Paneths Classification
   b) Other Classifications

4. Distinctions in naming Hydrides

5. Preparation of Hydrides
   a) Direct Union
   b) Reduction of Oxides with nascent hydrogen
   c) Hydrolysis
   d) Electrochemical

6. Physical Properties (Salt-Like Hydrides)
   Sp.G, Solubility, Conductivity, etc.....

7. Chemical Properties (Salt-Like Hydrides)
   a) Reaction with Halogens
   b) " " Oxygen and Sulfur
   c) " " Mercury
   d) " " CO_2, SO_2
   e) Action on H_2O
   f) Hydrides as Reducing Agents
   g) Stability toward Heat

8. Evidence for Existence of Salt-Like Hydrides

9. Electrolysis of Hydrides of Li, K, Na, Ca
   a) Molten Hydride alone
   b) " " dissolved in Eutectic Mixture of LiCl and KCl

10. ..resting Application of Hydrides

References:

1. Mellor: Comprehensive Treatise: Vol. 2, p. 481
2. " : " " : Vol 3, p. 649
3. Alexander: "Metals and Alloys", Vol.8, - 9 p. 263
4. Partington: Text Book of Inorganic Chem. p. 153
5. Bardwell: J.A.C.S. Vol. 44 p. 2499
6. Paneth: "Radio Elements as Indicators"
7. Stock and Kuss, Ber. Vol. 56 p. 789
8. Osburg: Monograph on Lithium: Theoretical Studies and Practical Applications
9. Moissan: Compt. Rend. Vol. 134 p. 71

E. B. Middleton

P_3 Cu' → Cu₂ P_3

Cu + Pop ≡

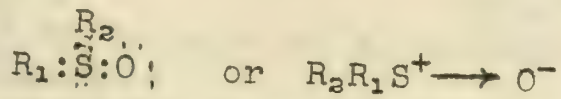
INORGANIC SEMINAR November 23, 1937

Optically Active Compounds Containing The Six Group Elements As Central Asymmetric Atom

In general a molecule exhibits optical activity when its atoms are arranged in such a way that the molecule does not have a plane, center or alternating axis of symmetry.

In carbon chemistry these requirements are met by placing in the 4 valence positions different radicals, either organic, or inorganic.

One of the first exceptions to the asymmetric conditions arose when a molecule such as $R_1R_2S = O$ was shown to be composed of stereo isomers thus the structure is best portrayed by



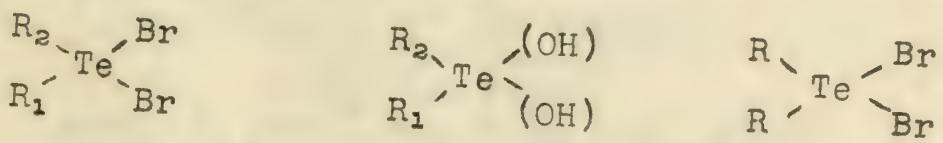
After the Sulfur compound above had been resolved, the study was extended to selenium and tellurium and compounds of the following types.

R_1R_2SOR R_1R_2SeO R_1R_2TeO

$R_1R_2R_3SX$

These also have been shown to possess the property of optical activity.

In tellurium series these molecules have been worked on and have given muta-rotating salts.



These compounds all contain the telluronium ion $(R_3Te)^+$. It is seen in example III that the asymmetry is further destroyed by having the "R" groups alike.

The evidence for the telluronium ion is supported by conductivity, hydrolysis and metathetical reactions of the dibromide. One bromine being much more active than the rest

References:

Lowry and Hüther Rec. trav. Chim. 55 688 (1936)
Ter Horst ibid 55 697 (1936)

M. W. Miller

12.35

1184.84

~~101.42~~

2

479.31
33 36
472.89
4.57

9900.7

2.90

822
21
61
01

137.24
55.00
27.4
28

11
153

454

385.57

527.28

142.25

94.45

28 18

1811.86

-1192.19

Paid dividend

Cash 30- 1271.71

Cash 30- 412.31

E. F. Frech

November 30, 1937

INORGANIC SEMINAR

RADIUM POISONING

I. Introduction
   A. Discovery of Radium - Becquerel's radium "burn" and sickness.
   B. Disintegration of radioactive substances - Radium series and mesothorium series.

II. Effects of Radium
   A. Radium "Burning
      Effects upon skin and tissures. - Reddening and blistering of skin.
   B. Radium Poisoning
      Cases of Radium poisoning of young girls working in watch factories. Necrosis of the jaw symptoms of poisoning, fixation of Radium in the body. Methods of getting Radium poisoning.

III. Detection of Radioactive substances
   A. Gamma-ray test
      The gamma-ray test indicates presence of a radio active substance but does not ell which of the many substances are present.
   B. Radon test
      This test proves the presence of Radium.
   C. Thoron test
      This test proves the presence of mesothorium

IV. Treatment of Radium Poisoning
   A. Various treatments - Ultra-violet light, Oxidizing colloidal solutions, etc.

References: Science 33 1001-5
J. Ind. Hyg. 7 371-82 (1925)
" " " 13 117 (1931)
" " " 15 433 (1933)
Amer. J. Pub. Health 23 1017 (1933)
J. Am. Med. Assoc. 66 1-6 (1916)
" " " " 85 1769 (1925)

Definitions

1. Quiescence - period of quiet - dormant period
2. Necrosis - Death of tissue and rotting away - softening and liquefaction
3. Leukocytosis - increase in leukocytes in the blood
4. Leukopenia - deficiency in the number of linkocytes
5. Lymphocytes - a lymph corpuscle
6. Lymphatic leucemia - leukemia of the lymphatic organs
7. Erythrocytes - red blood corpuscles
8. Leukocytes - white blood corpuscles
9. Mandibles - lower jaw
10. Lukemia - a fatal disease with a marked increase in the number of leukocytes in the blood.
11. Anemia - a condition in which the blood is deficient in either hemoglobin or red blood corpuscles.
12. Pernicious - tending to a fatal issue
13. Sepsis - poisoning by products of a putrefactive process
14. Terminal infection - an acute infection occurring near the end of a disease and frequently causing death.

Inorganic Seminar

December 7, 1937

METAL CARBONYLS OF THE SIXTH AND EIGHTH GROUPS

Since C. Langer's discovery of nickel carbonyl in 1888, many other carbonyls have been prepared; the most recently discovered member of this unique class of compounds is chromium carbonyl(1927).

I. Types of Carbonyls

1. Mono-molecular volatile carbonyls, very soluble in intert solvents.

$Fe(CO)_5$	$Ni(CO)_4$	$Ru(CO)_5$	(Liquids)
$Cr(CO)_6$	$W(CO)_6$	$Mo(CO)_6$	(Solids)

2. Bi- or poly-molecular carbonyls, non-volatile, insoluble in inert solvents

$Fe_2(CO)_9$	$[Fe(CO)_4]_3$	$Co_2(CO)_8$	solids
$Co_4(CO)_{12}$	$Ru_2(CO)_9$	$[Ru(CO)_4]_x$	solids

II. Structure of Carbonyls

It is generally accepted that the CO molecules are linked to the metal by coordinate bonds, $C \longrightarrow M$; evidently if the effective atomic number of the metal in the carbonyl is that of the next rare gas, the carbonyl will be volatile.

III. Preparation of Carbonyls

A general method of preparation is to heat the finely divided metal with CO; in some cases high pressure is necessary. The method fails entirely for $Cr(CO)_6$

IV. Preparation of Carbonyls by the Use of the Grignard Reagent

The hexacarbonyls of Cr, W, and Mo may be prepared by passing CO into a suspension of the anhydrous metal chloride in an organic solvent containing the Grignard reagent. Although the yields are small on account of side reactions, the carbonyls so prepared are very pure.

V. Ammine-Carbonyls

The CO molecules may be partly replaced by amine molecules to give such compounds as

$Cr(CO)_3Py_3$ $\quad$ $Cr(CO)_4Py_2$ $\quad$ $Cr(CO)_4C_{12}H_8N_2$

VI Technical Significance of the Carbonyls

Very pure metals may be obtained by thermal decomposition of the carbonyls, a method already in use commercially in the cases of nickel and iron. A study of the reactions of carbonyls may also explain the catalytic action of finely divided metals in certain reactions

References

W. Hieber Zeitschrift für Elektrochemie 43 (6) 390 (1937)
A. A. Blanchard Chemical Review 21 (1) 3 (1937)
Morgan and Burstall Inorganic Chemistry Chap. 17 (1937)
Manchot and Manchot Z. für Anorg. Allgem. Chemie 226 385 (1936)
Hieber and Romberg ibid 221 322 (1935)
Hieber and Mühlbauer ibid 221 337 (1935)
F. Hein J. für Praktische Chemie 132 59 (1931)
Hein, Reschke, Pintus Beinchte 60 749 (1927)

C. Rollinson

Inorganic Seminar December 14, 1937

EXPERIMENTING WITH ELEMENTARY F_2

I. Introduction
   a) This report covers the publications from one laboratory engaged in the study of elementary F_2. No attempt has been made to include publications from other laboratories.
   b) Description of generating unit

II. Publication No. 1. The Action of Elementary Fluorine upon Certain Aromatic Organic Compounds under Various Conditions
   a) Preliminary work to establish best conditions and equipment
   b) Description of reaction vessel chosen
   c) Fluorination of napthalene in CCl_4 at 0°. Positive results
   d) Fluorination of toluene in CCl_4 at 0°. Negative results

III. Publication No. 2. The Fluorination of Hexachlorobenzene
   a) Fluorination of hexachlorbenzene in CCl_4 at 0°. Positive results
      1. $C_6Cl_6F_4$
         $C_6Cl_6F_6$

IV. Publication No. 3. The Vapor Phase Fluorination of Hexachloroethane
   a) Description of apparatus
   b) Main product - sym-difluorotetrachloroethane

V. Publication of No. 4. The Vapor Phase Fluorination of Ethane
   a) Description of apparatus
   b) Products
      1) CF_4
      2) CHF_3
      3) C_2F_6
      4) Minor portion - Unidentified but believed to be either CH_3CF_3 or CH_2F_2

VI. Publication No. 5 - The Parachor of NO_2F
   a) Experimental. Prep. of Compound
   b) Consideration of results

VII. Conclusions

References

1) Bigelow and others J.A.C.S. 55 4614 (1933)
2) Same " 56 2773 (1934)
3) Same " 59 198 (1937)
4) Same " 59 2072 (1937)
5) Same " 59 2127 (1937)

Lee Whyte

INORGANIC SEMINAR DECEMBER 21, 1937

THEORY OF CHROMIUM DEPOSITION

I. Deposition of chromium from its lower valence states

A. The problem is essentially the same whether chromic or chromous salts are used.

B. Three reactions may occur at the cathode

1. $3Cr^{++} \longrightarrow Cr + 2Cr^{+++}$ (Insignificant)

2. $Cr^{++} + H^{+} \longrightarrow Cr^{+++} + 1/2\ H_2$ (Significant)

3. $Cr^{++} + 2\ominus \longrightarrow Cr$ (Significant)

C. The low hydrogen overvoltage of chromium makes it impossible to ever get good performance from such a plating bath.

D. It was thought that using complex chromic salts would permit operation in a more alkaline solution and hence improve plating conditions. This did not work out.

II. Deposition of chromium from the hexavalent state

A. Review of previous theories

1. $Cr^{+6} \longrightarrow Cr^{+3} \longrightarrow Cr^{+2} \longrightarrow Cr^{0}$

The role of the H_2SO_4 in the plating bath is to dissolve the film of basic chromium compounds that form around the cathode.

2. $Cr^{+6} \longrightarrow Cr^{+3} \longrightarrow Cr^{0}$

The Cr^{+3} is kept in a suitable ionized condition by the hexivalent chromium. The presence of the SO_4^{--} is also necessary for the favorable existence of the chromic ions.

B. Evidence that Deposition occurs directly from the hexivalent state

1. The behavior of the plating bath upon the addition of foreign ions could be used as evidence.

Since iron is not deposited to any great extent, it is difficult to see how under the same conditions chromium can be deposited from the trivalent state. That is, Fe^{+++} should give Fe^{0} easier than Cr^{+++} would give Cr.

ence of Cu^{++} in Cr^{+++} bath 2
ls everything, but
ence of Cu^{++} in $Cr_2O_7^{=}$ bath
o rad difference -- no Cu
es out, either.

C. Mechanism of Reduction.

1. It is possible to reduce negative ions such as Cr_2O_7 at the cathode under such conditions of alkalinity and potential that exclude the action of a hydrogen/hydrogen ion couple or chromous/chromic couple.

C. Mechanism of Reduction (continued)

2. Since the dichromate ion is negative, it will have a low interaction coefficient. The $Cr_2O_7^{--}$ ion because of its large size and negative charge will also have a high potential barrier. For these reasons, the deposition of chromium will require a very high polarization.

3. How is it possible that a powerful reducing agent, hydrogen, is liberated in the presence of a powerful oxidizing agent, chromic acid? It is postulated that the hydrogen is discharged internally in the metal.

4. Why is not copper deposited when present in the solution whereas hydrogen is deposited? No good reason is known. It is an observed fact that copper does not deposit on passive chromium.

References

Charles Kasper, B.S.J. Research, 9, 353 (1932) RP 476

Same " 11, 515 (1933) RP 604

Same " 14, 693 (1935) RP 797

A. R. Hanke

Cathode Cu or Brass	Temp	Optimum Current Density	Average Efficiency	Time required to deposit 0.005 mm	CrO_3 2.5 moles 250 g/l; $SO_4^{=}$ .05 N 25 g/l
	35°C	7.5	11	75 minutes	
	40	11.0	13	44	
	45	20.0	15	21	
	50	25.0	17	15	

Film of $Cr(OH)_3 \cdot CrOHCrO_4$ deposits under some conditions this prevents formation of Cr deposit. How does $SO_4^{=}$ prevent this? Baular says "by complexing" The author says $[CrO_4(SO_4)_4 \times H_2O]$

does it? This takes $SO_4^{=}$ to the negative pole where it can dissolve the film.

Inorganic Seminar January 11, 1938

SELENIFEROUS SOILS AND THE EFFECTS OF SULFUR ADDITION

I. Introduction

II. Work of Hurd-Karrer and Kennedy.
- A. The visible effects of selenium on plants
- B. Effect of sulfur and gypsum additions to wheat planted in soil treated with sodium selenate.
- C. Factors affecting absorption of selenium by plants.
  1. Whether in the form of selenate, selenite or in elementary form.
  2. Dependent upon tendency of the plant to absorb sulfur.
  3. Type of soil.
- D. Sulfur inhibition checked by toxicity of plant on rats.

III. Work of Williams and Byers on selenium compounds in soils.
- A. Analysis of 1000 soils showed maximum of 82 ppm. but normal amount of 1 - 6 ppm.
- B. Examination of soil with 22 ppm. of seleniun showed
  1. Very little removal by usual methods of extraction.
  2. All iron oxide and 95% of selenium removed by refluxing with 6N H_2SO_4.
- C. Results of tests to determine if iron oxide soils make selenium insoluble.
- D. Synthesis of various iron selenites.
- E. General conclusions concerning nature of selenium in soils.

IV. Work of Franke and Painter.
- A. Removal of selenium from toxic protein hydrolysates.
  1. All toxic selenium removed by butyl alcohol extraction.
  2. All selenium compounds precipitated by mercuric chloride.
- B. Effect of sulfur additions.
  1. Wheat and corn rotated in seleniferous soils treated with different amounts of sulfur and gypsum.
- C. Use of electrodialysis to determine available selenium.
  1. No soluble selenium material found in original soil.
  2. Selenium bound in soil treated with sodium selenite.
  3. Selenium bound in ashed soil treated with sodium selenite.

V. Conclusions

References

1. Hurd-Karrer	J. Agr. Research	49	343	(1934)
2. " "	Ibid	50	413	(1935)
3. Hurd-Karrer and Kennedy	Ibid	52	933	(1936)
4. Williams and Byers	Ind. Eng. Chem.	28	912	(1936)
5. Painter and Franke	J. Biol. Chem.	111	643	(1935)
6. Franke and Painter	Ind. Eng. Chem.	29	591	(1937)
7. Löddesol	J. Am. Soc. Agron.	24	74	(1931)
8. Robinson and others	Ind. Eng. Chem.Anal.	6	274	(1934)
9. Cheraskova and Veisbrute	Ibid	7	407	(1935)

Loring R. Williams

REDUCTION OF PERRHENANTES

I. Solid or fused perrhenates are reduced to rhenium metal when heated with H_2, C, CO, or NH_3. Fusion with stoichiometric am'ts of rhenium metal and rhenium dioxide yields rhenates, hyporhenates, rhenites and hyporhenites; ReO_4^{--}, ReO_3^{-}, ReO_3^{--}, ReO_2^{-}.

II.A- Electrolytic reduction of aqueous perrhenate solutions yields penta-, tetra-, and tri-valent rhenium; $ReOCl_5^{--}$, $ReCl_6^{--}$ and $ReCl_4^{-}$. In strongly acid solutions rhenium metal is quantitatively deposited.

B- Stannous chloride in the presence of CNS^{-} and HCl reduce perrhenates to $ReO(CNS)_4$ or $ReO(CNS)_6^{--}$. This is the basis of the colorimetric determination of rhenium.

C- Concentrated HCl and HBr reduce perrhenates to $ReOX_5^{--}$ when heated in a sealed tube to 200° C. When equivalent am'ts of K_2ReCl_6 and $KReO_4$ are heated in a sealed tube, K_2ReOCl_5 is formed.

D- Perrhenates dissolved in conc. H_2SO_4 are reduced by SO_2 and organic reagents to a blue compound which is said to be Re_3O_8.

III. A. Reduction of weakly acid perrhenate solutions with zinc metal yields $ReO_2.XH_2O$. This was used as a gravimetric procedure, but has been shown to be unsatisfactory by Geilman and Hurd. Young and Irvine have shown that $Re_2O.2H_2O$ is formed as 25% of the reduction product. It is a black insoluble material which is dissolved by nitric acid and bromine water, but which is not dissolved by conc. hydrochloric acid, conc. sodium hydroxide, alkaline sodium chromate or acid ferric sulfate.

Reduction of perrhenate by cadmium metal under the same conditions yields $ReO.H_2O$ which has the same properties as $Re_2O.2H_2O$.

B. When a cold (5°C) weakly acid solution of perrhenate is passed through a column of amalgamated zinc, Re^{-I} is formed. The reduced solution will reduce Cu^{II} and Ag^{I} to the metal, Ti^{IV}, to Ti^{III}. When heated to 50° C. with sulfuric acid, reduced compound is oxidized to Re^{I}. Re^{I} has a yellow color in sol'n. and is not very stable. Neither Re^{-I} nor Re^{I} is volatile.

References

1. Heyne and Moers, Z. Anorg. Allg. Chem., 196, 143 (1931)
2. I. and W. Noddack, ibid, 215, 129 (1933)
3. H. Hölemann, ibid, 211, 195 (1933)
4. Jacob and Jezowska, ibid, 220, 16 (1934)
5. J. G. F. Druce, Rec. trav. Chim., 54, 334 (1933)
6. Briscoe, et al, Jour. Chem. Soc., 2263 (1931)
7. Young and Irvine, J. Am. Chem. Soc. 59, 2648 (1937)
8. Lundell and Knowles, J. Research Nat. Bur. Standards, 18, 629 (1937)

Grieff
McKeever
Robinson
Spence

1-2 Sec 7
Sec 60

Witte
Langdon

Inorganic Seminar

January 18, 1938

HELIUM IN NATURAL GAS

I. Historical

(a) Helium was first discovered spectroscopically in the sun in 1868 by Lockyer and on the earth in 1895 by Ramsay.

(b) This gas was subsequently found to be a minor constituent of many minerals, rocks, etc.

(c) Cady and McFarland in 1903 discovered presence of large quantities of helium in natural gas fron numerous localities of Kansas.

(d) War emergency stimulated search for helium and means of extracting for use in lighter-than-air craft.

II. Occurrence of Helium.

(a) Helium occurs in many minerals and rocks, in natural gas wells, coal and metal mine gases, mineral springs, volcanic and fumarole gases, and in the atmosphere. It has been identified in the spectra of a great many stars and is abundant in the nebulae.

(b) Georgraphically, natural gas wells carrying noteworthy amounts of helium are located near Amarillo, Texas; Petrolia, Texas; southeastern Kansas and northern Oklahoma; southern Ohio; southeastern Colorado; Utah; California; and Alberta, Canada.

So far as known, the United States possesses the only supply of helium in sufficient quantity to warrant its extraction on a commercial scale.

(c) Geologically, the helium reservoirs are situated generally in porous strata in areas of favorable geologic structure. The age of the helium-producing formations ranges from Cambrian to Tertiary. While not always the case, a great many of the rich helium gases occur in reservoirs lying close to the crystalline basement rocks.

III. Theories of Origin and Accumulation.

(a) Derivation through radioactivity.
(b) Primordial helium
(c) Atmospheric origin

Theory (a) is most universally accepted, yet difficulties are encountered in attempting to apply this theory to all helium-rich gases.

IV. Commercial Production

(a)

(a) Helium recovery plants have been erected and operated at Ft. Worth, Texas; Petrolia, Texas; Dexter, Kansas; Model Dome, Colorado; and Amarillo, Texas. By executive order of

March 31, 1924, the entire area of the Woodside anticline, Utah, was set aside by the United States as Helium Reserve No. 1. The Petrolia field is now practically depleted. The Amarillo region is most productive at the present time.

(b) Three principal processes of gas liquefaction and distillation have been employed in extracting helium from natural gas:

1. Linde process
2. Claude process
3. Jeffries-Norton process

At present a modified process is being used.

(c) The capacity of the Amarillo plant is two million cubic feet of helium per month, and at present the net operating cost averages about $7.50 per thousand cubic feet, the purity of the product being more than 98%.

V. Uses of Helium.

Helium is used for lighter-than-air craft, decompression for underground workers, alleviation of asthmatic conditions, metallurgical processes, filling of interior of nautical and scientific instruments, cryogenic purposes, and as a cooling blanket for high speed dynamos.

REFERENCES

1. Minerals Yearbook (1937)
2. Information Bulletin, U.S. Helium Plant, Amarillo, Tex. (1936)
3. "Geol. of Nat. Gas" (Symposium), A.A.P.G., 1053 (1935)
4. U.S. Bur. Mines, Information Circular 6745 (1933)
5. Seibel, Chem. and Met. Eng. 37, 550 (1930)
6. Ruedemann and Oles, Bull. A.A.P.G. 13, 799 (1929)
7. Rogers, Prof. Paper 121, U.S. Geol. Survey (1921)
8. Cady and McFarland, Am. Chem. Soc. J. 29, 1524 (1907)

R. N. Keller

Inorganic Seminar

February 15, 1938

THE CHELATE RINGS

(Abstract)

The term "Chelate" (kē-lāte) designates the cyclic structures which are formed from the union of metallic atoms with organic molecules. The formation of these rings may involve either primary or secondary valence or both.

If the metal atom is linked to the organic molecule through one group, the chelate is of the is of the unidentate class; two groups -- bidentate; three groups tridentate: etc. The bidentate group is the most important.

Among all the classes the valence of the complex radical is equal to the valence of the central metal atom minus the number of primary valence groups held in the coordinating groups in the coordination sphere by acidic groups leads to a series of compounds, the complex ions of which have successively changing ionic charges.

Among the organic groups that unite with metals by the replacement of hydrogen are the following:

$-COOH$	$-\overset{H}{\overset{\vert}{N}}H$ (primary amino)
$-SO_3H$	$-\overset{R}{\overset{\vert}{N}}-H$ (secondary amino)
$-OH$ (enolic hydroxyl)	
$-N\begin{smallmatrix}H\\O\end{smallmatrix}$ (oxime)	

The groups which may unite with the metals by secondary valence are:

$-\underset{\vert}{N}H_2$ (primary amino)	$=NOH$ (oxime)
$-\underset{\vert}{N}H$ (secondary amino)	$-OH$ (alcoholic hydroxyl)
$-N-$ (tertiary amino)	$=O$ (carbonyl)
$=N'$ (cyclic tertiary amino)	$-S-$ (thioether)

The evidence for chelation is the following:

1. While the coordination number of the certain metals is invariably four or six in many cases of unidentate compounds, only two or three molecules of organic compounds bearing two associating units unite with such metals. Therefore, ring structure must be assumed if all the coordination positions are to be occupied.

2. Analytical tests for metals on solutions of their complex salts fail. This shows the absence of simple metallic ions. conductivity and migration experiments prove the complex to be a non-electrolyte, anion, or cation.

3. The compounds are saturated and incapable of further addition.

4. Predictable isomeric phenomena have been realized.

5. Compounds made asymmetric by chelation have been, in many instances, resolved.

6. Groups involved in chelation are non-reactive.

7. Chelates are formed only when rings from four to seven members are possible.

8. When a chelate ring is broken by double decomposition, the chelating groups enter in reactions.

Reference: Diehl, 4, Chem. Rev. 21, 39-111 (1937)

Jacob Kleinberg
February 15, 1938

This abstract has been taken almost word for word from various parts of Diehl's paper. It was thought best to do this in order that a clear and concise summary might be given.

Inorganic Seminar

FERRITES

February 22, 1938

Three distinct series of compounds of irom are known to exist, where iron united to oxygen and forms a characteristic anion.

1. Salts of $HFeO_2$ (Sepedocrocite) called ferrites (occur naturally and also may be prepare synthetically)

2. Salts of hypothetical H_2FeO_3 called ferrates
3. " " " H_2FeO_4 " perferrates
(2-3 do not occur in nature)

The ferrites can be prepared in the following manner: Fusing the two oxides in correct proportions at temperatures around 1000°; Fusing the carbonate of the cation metal with Fe_2O_3; Co-precipitation of the hydroxides if they are both insoluble and then sintering as above; precipitation, from a soluble ferrite of an insoluble ferrite. By the above methods ferrites of all the common cations have been prepared.

The actual existence of many of the ferrites of the heavy metals (Pb-Mn-Cu-Ni-Co-) have not been completely confirmed due to insolubility and also because they always have present as impurities excess of Fe_2O_3 or MO. (M = divalent metal.

Because the ferrites are strongly magnetic like magnetite $Fe(FeO_2)_2$ - studies of the magnetization curves in relation to % composition gives diagrams similar to phase diagrams and indicates compound formation in molar ratios of $MO:Fe_2O_3$ of 1:1.

Similar studies by Röntgenographic means also show the ferrites to have similar structures and compares with those of the magnetization data.

(1) The Ferrites are similar to the spinels in that they are capable of dissolving and forming solid solutions of ferrite and Fe_2O_3

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M.W. Miller

New Metallurgy of Magnesium

Science - Oct 22, 1937

Page 10 of supplement

$MgO + C \longrightarrow Mg + CO$

$Mg \rightarrow$ chill with H_2 to condense

$\overset{+2}{Fe}(\overset{+3}{Fe}O_2)_2$

Inorganic Seminar - March 1, 1938

SOME RECENT WORK ON TITANIUM AND ZIRCONIUM

I. Introduction

II. Summary of the properties which make metallurgy difficult

III. Summary of common methods of reduction and disadvantages.
- (a) Titanofluorides by sodium or potassium.
- (b) Titanium tetrachloride with hydrogen or sodium.
- (c) TiO_2 with metals like Mg, Al and Si.
- (d) TiO_2 with carbon at high temperatures.
- (e) TiO_2 with calcium shavings.
- (f) Electrolysis of TiO_2 in fused $CaCl_2$.

IV. Description of work done by W. Kroll.
- (a) Apparatus.
- (b) Procedure
  1. Mixture of purified TiO_2, calcium shavings and $CaCl_2/BaCl_2$ (75/25) heated in furnace to 1000° in atmosphere of argon.
  2. Further reduction with mixture of calcium, calcium hydride and $CaCl_2/BaCl_2$ at 1000° in atmosphere of argon.
  3. Attempts to remove last traces of oxygen.
  4. Properties of metals obtained
  5. Conclusions from experimental work.

V. General Conclusionsl

References

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Loring R. Williams

[illegible]

INORGANIC SEMINAR - March 8, 1938

THE FLUOROCHLORIDES OF SILICON AND GERMANIUM

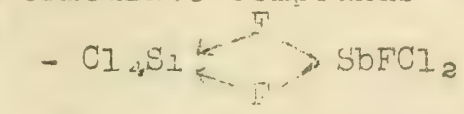
I. Introduction
The Swarts Reaction: Reaction of Antimony trifluoride and an non-polar halide with pentavalent antimony as a catalyst.

II. Fluorochlorides of Silicon
(a) Method I. Action of Chlorine upon hexafluorosilane.
(b) Method II. The Swarts reaction
(c) Properties of the fluorochlorosilanes

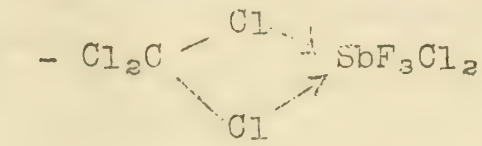
III. Fluorobromides of Silicon
(a) Method I. Action of bromine upon hexafluorosilane
(b) Method II. The Swarts reaction
(c) Properties of the fluorobromosilanes

IV. Chlorofluorides of Germanium
(a) Preparation of Swarts reaction
(b) Properties

V. Mechanism of the Swarts reaction
(a) Three classes of reactions
1. Non-polar halides, covalently unsaturated
2. Non-polar halides, covalently saturated
3. Non-polar halides, not reacting
(b) Types of intermediate compounds
1. Type A



2. Type B



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Emil F. Frech

Inorganic Seminar - March 15, 1938

INVESTIGATIONS CONCERNING THE RADICAL HO_2 IN SOLUTION, AND THE INTERACTION OF OZONE WITH HYDROGEN PEROXIDE

I. Investigations of the Radical HO_2 in Solution.

(A) Formation of the Radical in Reactions with Molecular Oxygen

1) Existence first assumed by Haber to explain the combustion of atomic hydrogen with molecular oxygen.

2) Used to explain the catalytic decomposition of H_2O_2 in solution

$$HO_2 + H_2O_2 = H_2O + OH + 18 \text{ K. Cal}$$

(B) Spectroscopic Investigations of the Radical HO_2 in Solution

(C) Decomposition of Ozone in aqueous Solution.

1) The decomposition of O_3 in aqueous solution is catalyzed by OH ions

$$O_3 + OH^- = O_2 + HO_2$$

II. The Interaction of Ozone and H_2O_2 in Aqueous Solutions.

(A) The Work of Rothmund and Burgstaller

1) H_2O_2 is an efficient catalyst for the decompostion of Ozone: $2O_3 = 3O_2$

2) Large excesses of H_2O_2 give this reaction

$$H_2O_2 + O_3 = H_2O + 2O_2$$

(B) Intermediate Compounds

1) Choice lies between H_2O_3 and HO.

2) HO_2 might possibly be an intermediate

(C) Decomposition of HO_2

1) $2HO_2 = H_2O + O_3$

(D) Decomposition of Ozone

1) Slow in dilute acids at low temperatures

2) Increases as OH^- ion concentration increases

(E) Energy Relations

The decreases of free energy in the intermediate reactions are estimated

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E. B. Middleton

Inorganic Seminar - March 22, 1938

Higher Oxidation States of Silver

Solutions of bi- and trivalent silver can be prepared by oxidation of solutions of univalent silver salts by such strong oxidizing agents as ozone, potassium peroxysulfate, bismuthic oxide, lead dioxide, and fluorine, and also by anodic oxidation. These argentic solutions are powerful oxidizing agents and can oxidize manganous ion to permanganate, chromium to chromate, iodate to periodate. The oxidizing power is due to the presence of a higher valence state of silver and not to peroxides.

The oxidation state of the silver in solution is the bivalent, but an equilibrium is set up between the bivalent silver and the tri- and univalent:

$$2Ag^{++} + H_2O = AgO^+ + Ag^+ + 2H^+$$

When the solution of bivalent silver is diluted, basic salts of trivalent silver precipitate. The oxidation potential of bivalent silver is 1.94 volts, which places it between ozone and hydrogen peroxide in oxidizing strength.

Both bi- and trivalent silver salts can be obtained from the solution of bivalent silver. AgS_2O_8, 4Pyridine and similar salts have been obtained; $AgONO_3$, Ag_2O_3, 4AgO can be obtained by dilution of a nitric acid solution of the bivalent salt or as a deposit at the anode in the electrolysis of a neutral solution of silver nitrate.

Two pure compounds of bivalent silver have been prepared; AgO, by boiling the nitrate complex, given above, with water, and AgF_2, by passing fluorine over heated silver metal or halide.

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E. O. Brimm

HYDRIDES OF PHOSPHORUS WITH SPECIAL REFERENCE TO P_2H_4 and "$P_{12}H_6$"

The following hydrides of phosphorus are reported in the literature: PH_3(gaseous), P_2H_4 (liquid), $P_{12}H_6$ (yellow solid), P_4H_2 (orange solid), P_5H_2 (solid), P_2H_3 (crystalline), and P_3H. With the exception of PH_3, the structures of none of these hydrides have been proved beyond question.

I. Phosphone (PH_3)

Pure PH_3 is said to ignite spontaneously in air if very dry. It has long been recognized, however, that the spontaneous inflammability of PH_3 as usually prepared is due to traces of a liquid phosphorus hydride, P_2H_4.

Phosphine would be expected to form partially halogenated compounds analogous to those formed by the hydrides of N, B, C, Si, and Ge. However, attempts to prepare such compounds have been unsuccessful.

II. Liquid Phosphorus Hydride (P_2H_4)

An exact molecular weight determination was made of this substance and the formula P_2H_4 verified. The molal heat of vaporization was calculated to be 7890 cal.; the boiling point, by extrapolation, 51.7° C.; and the freezing point -99°C.

Attempts to prepare a hydrochloride of P_2H_4, analogous to the hydrochloride of hydrazine, were unsuccessful.

The decomposition of liquid phosphorus hydride may be formulated to take place in such a manner that amorphous phosphorus and PH_3 are formed first:

$$3P_2H_4 \longrightarrow 4PH_3 + 2P \text{ (amorphous)}$$

The so-called solid yellow hydride "$P_{12}H_6$" which results is said to be due to the adsorption of PH_3 on the amorphous phosphorus.

III. Solid Phosphorus Hydride ("$P_{12}H_6$")

The solid phosphorus hydride obtained by the decomposition of P_2H_4 is variable and not stoichiometric in composition; therefore, it is not justifiably represented as a definite compound $P_{12}H_6$. X-ray studies indicate an amorphous structure, and the solid hydride is regarded as a sorption complex of PH_3 on a yellow amorphous form of phosphorus. PH_3 is evolved on heating, but there is no escape of hydrogen at temperatures below the dissociation temperature of PH_3.

Depending on the manner of preparation, a product can be obtained which varies in composition from $P_{12}H_{4.3}$ to $P_{12}H_{7.2}$.

Addition of substances less volatile than PH_3, such as ammonia, piperidine, or alkaylated phosphines, causes part of complete escape of the hydrogen as pure PH_3, and the phosphorus is transformed into a form of smaller surface area.

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R. N. Keller

$$\overset{-4\frac{1}{2}}{P_9H_2} \longrightarrow \overset{-2\frac{1}{2}}{P_5H_2} + \overset{-3}{P}H_3$$

$P_{12}H_6$

$$\begin{array}{r} 12 \\ \times \\ \hline 37\frac{1}{2} \\ 6 \\ \hline 378 \end{array} \qquad \begin{array}{r} 1\frac{1}{2} \\ \hline 6.000 \\ 378 \\ \hline 2220 \end{array}$$

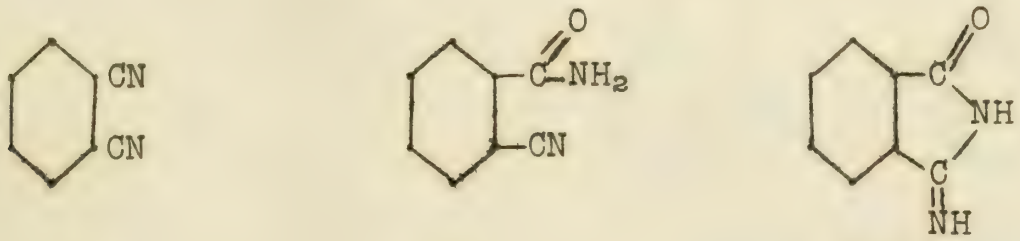
PHTHALOCYANINE PIGMENTS AND RELATED COMPOUNDS

Linstead -- Imperial College of Science and Technology, London
Halberger - Org. Chem. Institute der Technischen Hochscule, München

In 1927 de Diesboch and Von der Weid, while attempting to prepare phthalonitrile from o-dibromobenzene and cuprous cyanide, obtained instead of the expected nitrile, a deep blue, insoluble, very stable complex of the following composition, $C_{32}N_8H_{16}Cu$. This reaction, because it was not considered important at that time, was forgotten until Linstead began the study of the phthalocyanine pigments.

Linstead's original compound was a deep blue, iron complex obtained as a by-product in the synthesis of phthalimide from phthalic anhydride in the presence of iron.

The first investigation was on the possible dehydration and rearranged products of the phthalimide synthesis.



I II III

Phthalonitrile (I), o-cyanobenzamide (II) and imino phthalimide (III) all react in an exothermic reaction with metals or metal salts (carbonates, oxides, hydroxides, halides and sulfides) to form similar complexes if the metal is different and the same complex if the same metal is employed. The derivative obtained from copper is identical with that of de Diesboch and Von der Weid.

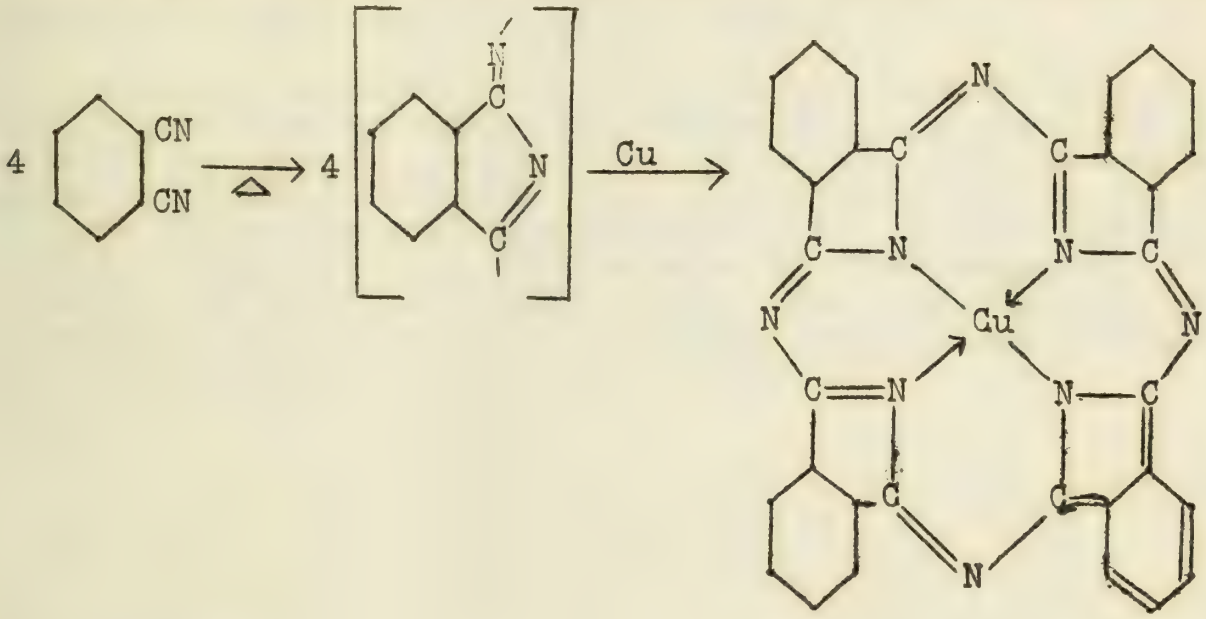
The reaction is still more general, 1,2- and 2,3-dicyanonaphthalenes undergo the reaction dissolving the massive metals to form naphthocyanines. Likewise o-dicyano pyridone, o-dicyanothiophen and $\alpha\alpha'$-diphenyl maleic nitrile also react.

The metal-free phthalocyanine itself is a deep blue, very stable compound of the composition $(C_{32}N_8H_{16})H_2$ and can be prepared dissolving the magnesium derivative in concentrated sulfuric acid, then pouring the resulting solution on ice.

The metallic derivatives possess a remarkable stability which makes them ideal for paint pigments. They are unaffected by concentrated sulfuric acid, molten alkalies, mild oxidizing and reducing agents, concentrated hydrochloric acid and light. Vigorous oxidizing agents decompose them into phthalimide-metallic salts and nitrogen. Dry distillation with soda-lime gives benzonitrile and ammonia. They may be heated in air to temperatures around 300° C without being oxidized and sublimed at temperatures above 500° C in an inert atmosphere and low pressure.

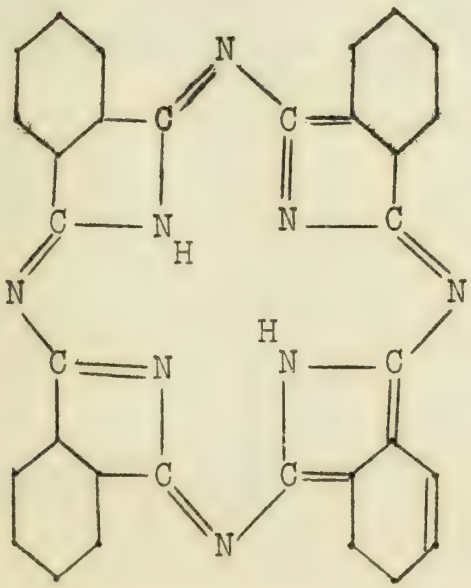
Linstead proposed a porphyrin-like structure for these compounds on a basis of their similarity to the natural pigments such as chlorophyll and haemin. The natural and synthetic pigments have similar stabilities, colors, derivatives, etc.

The ease of formation of a porphyrin-like ring having four -N= bridges instead of $-\overset{H}{C}=$ is shown for the copper derivative.

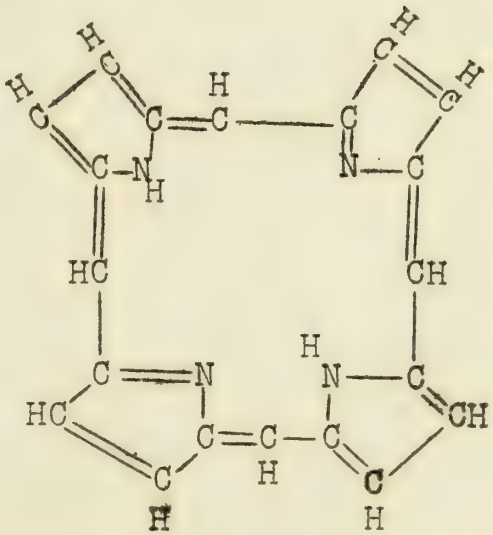


Copper phthalocyanine
Copper tetra benzo tetra azaporphin.

The structure of phthalocyanine as compared to porphyrin is shown in the two following diagrams.



Phthalocyanine
tetra benzo tetra
azaporphin



Porphyrin

Phthalocyanines are now named as porphyrin derivatives. The prefix aza indicating a=N-1 bridge. Thus the metal-free pigment is tetra benzo tetra azaporphin.

An extension of the condensations has been to prepare molecules containing the methine bridges.

Dent has prepared from methylene phthalimide, phthalonitrile and copper, a green copper tetrabenzo-triazaporphin. Halberger by reacting o-bromo acetophenone and cuprous cyanide has obtained copper tetrabenzo-monoazaporphin and by carrying out the condensation in the presence of phthalonitrile the diazaporphin can be formed. Halberger also has isolated by chromatographic adsorption on Al_2O_3 the iron tetrabenzoporphin. The last compound was formed in small amounts along with the diaza- and monoazaporphins from o-cyanoacetophenone and metallic iron.

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Reported by M. W. Miller
April 6, 1938.

Inorganic Seminar April 12, 1938

OXIDES OF LEAD AND LEAD COMPOUNDS

I. Introduction

II. Oxides of Lead

A. The existence of the following oxides of lead is undisputed, (1)

1. PbO - two modifications
2. Pb_3O_4
3. PbO_2

B. X-Ray and Chemical Analysis show that PbO, Pb_3O_4 and PbO_2 may contain various amounts of O_2 without any change in the lattice (1) (2)

1. The PbO lattice persists thru a range of composition from PbO to $PbO_{1.1}$
2. As more O_2 is taken on a new lattice appears at $PbO_{1.13}$ and persists to $PbO_{1.66}$. The color changes from clay yellow ($PbO_{1.13}$) to dark brown ($PbO_{1.28}$) to black borwn ($PbO_{1.30}$) to brown black ($PbO_{1.33}$ to $PbO_{1.66}$)
3. PbO_2 will give up oxygen down to $PbO_{1.66}$ without a lattice change, but cannot be forced to absorb O_2.

C. The existence of the following oxides of lead is disputed:

Pb_2O
Pb_2O_3 (4)
Pb_4O_5
Pb_5O_8
Pb_2O_5

(3)

III. Basic Sulfates of Lead.

A. The following basic sulfates of lead prepared at low temperatures have been reported:
$2PbO.PbSO_4$, $PbO_2.2PbSO_4$, $3PbO.PbSO_4$, $PbO.2PbSO_4$, $4PbO.PbSO_4$

B. Approximately 200 preparations of the basic lead sulfates prepared at low temperatures were made by Schieltz, and the three basic sulfates $2PbO.PbSO_4$, $3PbO.PbSO_4$, and $4PbO.PbSO_4$ were the only ones found.

IV. A new lead - sodium - oxygen compound was prepared.

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W. M. Shafer

Inorganic Seminar April 19, 1938

The Reciprocal Salt-Pair $(NH_4)_2SO_4 + 2KCl \rightleftharpoons K_2SO_4 + 2NH_4Cl$ in H_2O and in NH_3-H_2O at 25° respectively.

Various processes suggested for increasing the production of Potassium containing compounds involve the separation of that element from associated salts by fractional crystallization. The only satisfactory method of obtaining a clear understanding of the possibilities of making such separations, industrially according to Blasdale (2), is to make a study of the phase rule diagrams representing the equilibrium which exists in aqueous solutions between the salts to be separated.

The four three compoent systems concerned in the above reaction have been studied before but no comparisons made of the results from two different solvents under similar conditions according to Hill and Loucks (1).

Patridge and Gabriel (3) prepared KOH from Polyhalite by making use of the reaction between $(NH_4)_2SO_4$ and KCl to precipitate K_2SO_4 from an aqueous solution saturated with NH_3 in which liquid K_2SO_4 is very soluble.

System KCl - K_2SO_4 gives the solubility of the two separate salts and the composition of the invariant solution saturated with both.

System $K_2SO_4(NH_4)_2SO_4$ shows that the solid phase is a continously varying solution, the composition of which is in equilibrium with various solutions as appear in diagrams.

System $(NH_4)_2SO_4$ - NH_4Cl gives the solubility of the two salts and the composition of the invariant solution.

System NH_4Cl-KCl-H_2O outlines the invariant solution which is saturated with two limiting solid solutions for which the composition is given.

The solid phases existing are three solid solutions (1) NH_4Cl containing KCl up to a maximum of 2.5%, (II) KCl containing NH_4Cl up to a maximum of 16.6% and (III) K_2SO_4-$(NH_4)_2SO_4$ in all ratios.

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J. H. Touchstone

April 29, 1938

INORGANIC SEMINAR

"DIPOLE MOMENTS"

I. Measurement of the dipole moment ---the methods employed depend almost wholly on the determination of the dielectric constant.

1. Under the influence of a field, the molecule may undergo three types of polarization
   a. electronic
   b. atomic
   c. orientation

2. The expression relating polarization and dipole moment is that deduced by Debye

$$P = \frac{\varepsilon - 1}{\varepsilon - 2} \cdot \frac{M}{D} = \frac{4\pi N}{3}\alpha + \frac{4\pi N}{3}\frac{\mu^2}{3RT}$$

II. Moments of type inorganic molecules

1. The rare gases and diatomic elementary gases

2. Diatomic molecules of the type AB, such as HCl

3. Triatomic molecules of the type AB_2, such as HOH

4. Tetratomic and pentatomic molecules of the type AB_3 and AB_4, such as NH_3 and CH_4

III. Miscellaneous considerations

1. Coordination and the dipole moment
   a. The moments of some coordination compounds of the halides of beryllium, boron and aluminum

   b. The moments of organic compounds known to contain coordinate links, e.g., diphenyl sulphoxide and diphenyl sulphone

2. Organic compounds and the dipole moment.

   a. Moments of cis-trans compounds

   b. Moments of the azo compounds

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V. F. Balaty

Modern Tanning

I Introduction

Chromium salts and vegetable tannins are the most widely used tanning agents. Combination chrome-vegetable tanning is used successfully for some types of leather.

This report includes a description of the actual practice of chrome tanning as carried out in a typical American tannery and a discussion of the mechanism of reaction between hide substance and basic chromium salts.

The writer is indebted to the Moench Tanning Co., Gowanda, N.Y. (branch of Brown Shoe Co.) for samples of leather illustrating the tanning process.

II Chrome Tannery

(1) Hide house - Sorting, trimming, weighing hides into packs.
(2) Beam house - Soaking, washing, liming, unhairing, fleshing, bating, pickling.
(3) Tan room - Preparation of chrome liquor, tanning.
(4) Splitting room - Pressing, wringing, setting out, sorting, splitting, shaving.
(5) Color room - Dyeing, fat-liquoring
(6) Drying department - Setting-out, rough-drying, sammying, toggling (or tacking); or pasting as alternative to rough-drying and toggling.
(7) Finishing department - Application of colored finishes, waxes, etc., and various mechanical operations as rolling, glazing, boarding, printing, etc.

III Chrome Tanning - Theory

The pickled hides to be tanned are fairly pure collagen containing considerable mineral acid.

The chrome liquor at the start of the tanning process is usually 33 1/3% basic and contains polynuclear Cr complexes of fairly small particle size which easily penetrate the hide. Addition of $NaHCO_3$ increases the basicity, and the particles increase in size (on account of olation) until a basic Cr salt is deposited on the hide fibres.

The process of olation is indicated by the following equations:

(1) $[(H_2O)_6Cr]_2(SO_4)_3 \rightleftharpoons 2[(H_2O)_5Cr(OH)]SO_4 + H_2SO_4$

(2) $2[(H_2O)_5Cr(OH)]SO_4 \longrightarrow [(H_2O)_4Cr \overset{O}{\underset{H}{\rightleftharpoons}} Cr(H_2O)_4](SO_4)_2 + 2H_2O$

Continuation of this process leads to large aggregates. Removal of acid by $NaHCO_3$ shifts equilibrium (1) to the right, thus favoring olation.

Stiasny points out that neither simple ionic Cr salts nor colloidal basic Cr salts have tanning properties while partially olated polynuclear Cr compounds are tanning agents.

The question as to whether an actual chemical combination takes place between hide substance and basic Cr salts has not been finally answered.

McLaughlin and co-workers have shown that the course of chromium take-up follows a Freundlich adsorption isotherm. Their conclusions may be summarized as follows:

(1) The driving force in chrome tanning is the ability of hide substance to combine with and remove acid from the tan liquor;

(2) The equilibrium existing between the protein-~~borenal~~ bound acid of the leather and the free or potentially free acid of the liquor establishes and regulates the equilibrium between Cr salt fixed by the hide and that remaining in the liquor.

(3) Chrome tannage is completely reversible.

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Chem. Eng. Dept. - Lehigh

C. L. Rollinson

RECENT WORK ON PLATINOUS-OLEFIN AND PALLADOUS-OLEFIN COMPOUNDS

I. Introduction

All methods of explaining the coordination compounds of unsaturated hydrocarbons with divalent platinum by electron pairs are artificial. The unsaturated hydrocarbon, which is represented to be the donor atom, has no lone pair of electrons.

II. Compounds of type $K[PtX_3 . C_nH_{2n}]$

A. Preparation

1) Reaction of olefin with potassium chloroplatinite
2) Reduction of potassium chloroplatinate with the corresponding alcohol
3) Direct replacement of one olefin by another

B. Reactions

1) $K[PtCl_3.Uns] + 4KCN \longrightarrow K_2Pt(CN)_4 + Un + 3KCl$
2) $K[PtCl_3.Uns] + H_2O \longrightarrow KCl + 2HCl + Pt + CH_3CHO$
3) $K[PtCl_3.Uns] + C_5H_5N \longrightarrow PtCl_2.2\cancel{Uns}C_4H_5N + Uns$

III. Compounds of type $[UnsPtCl_2]_2$

A. Preparation

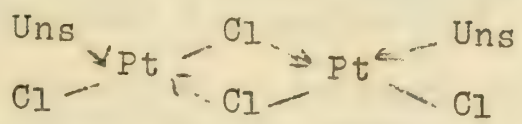
1) Reaction of potassium chloroplatinate with alcohol
2) $Un + PtCl_2$
3) $Un + PtCl_4$
4) Replacement of one olefin by another

B. Reactions

1) $[UnsPtCl_2]_2 + 4C_5H_5N \longrightarrow 2Uns + 2Pt(C_5H_5N)_2Cl_2$ (trans)
2) $[UnsPtCl_2]_2 + 4HCl \longrightarrow 2Uns + {}_2H_2PtCl_4$
3) $[C_2H_4PtCl_2]_2 + 4H_2 \longrightarrow 2Pt + 2C_2H_6 + 4HCl$
4 $[UnsPtCl_2]_2 + 2Br_2 + UnBr_2 + PtBr_2$
5. Replacement by other olefins
6.

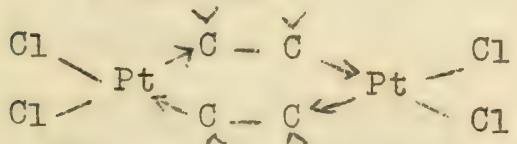
C. Proposed Structures

1)



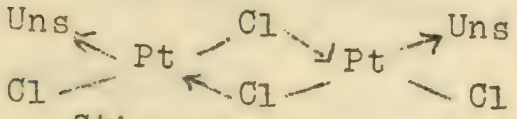
Pfeiffer

2)



Kharasch and Ashford

3)



Stiegman

IV. Compounds of type $[UnsPdCl_2]_2$ Only successful method of preparation: $PdCl_2 + 2C_6H_5CN \longrightarrow [(C_6H_5CN)_2PdCl_2 \xrightarrow{2Uns} [UnsPdCl_2]_2 + 4C_6H_5CN$

References: (1) Anderson, J. Chem. Soc., 971 (1934; 1042 (1936)
(2) Kharasch and Ashford, J. Am. Soc. 58, 1733 (1936)
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(4) Kharasch, Seyler and Mayor, J. Am. Chem. Soc., 60, 882 (1938)
(5) Gel'man, Sci. Repts. Leningrad State Univ. 2, No. 2, 5-47 (1936); C.A. 32, 3505 (1938

Jacob Kleinberg

$[P_1 X_2 \text{trans}]_2 + py \Rightarrow [P_1 X_2 py_2]$

Is this cis or trans?

Kharasch & Ashford's formula demand that it be cis

Actually it is trans — See CA 32, 445 1193

Inorganic Seminar November 5, 1938

STRUCTURE OF THE COPPER LAKES OF AZO-DYES

Topic I

Introduction:

Lake formation with copper increases the stability of azo-compounds, particularly toward light, but little is known to account for the effect.

The stability of the lakes is enchanced among those which have inner coordination of copper with azo-nitrogen, such forms arising only when copper is affixed by covalent linkings to substituents (such as OH, COOH, or NH_2) which are in the o-position to the azo-groups, m- or p-hydroxyls having little or no effect; the presence of two substitutents of this kind (particularly two hydroxyl groups) in the o,o'-positions further increases the stability, the lakes assuming fused-ring forms.

Data seem to indicate at the stable coordination compounds of cupric copper are ordinarily those in which the copper atom is associated with 35 planetary electrons (i.e., the atomic number of copper, together with 6 additional electrons from attached atoms), but that in the copper lakes of azo compounds this number of electrons may fall short of 35 by one or more pairs. When this occurs, the lake will exhibit co-ordination unsaturation and will tend to combine with one or more molecules of water, ammonia, or the like. Further, when water and the like are present in the lake, the number of associated planetary electrons may in rarer instances be exceeded by one or more pairs, in which case the lake will tend to lose co-ordinated molecules until the number of electrons associated with the copper atom has reached 35.

The azo group of aromatic substances shows, apparently, little or no co-ordinating power for a metal atom not already attached by some other group in an o-position to the azo-group.

o-Hydroxy-azo-compounds:

These substances contain one copper atom to two azo groups; they are co-ordinatively saturated; structural considerations indicate that the copper atom, whether planar or tetrahedral, cannot be co-ordinated with both nitrogen atoms of an azo group.

o-Carboxy-azo-compounds:

An o-carboxyl group in azobenzene resembles an o-hydroxyl, but occasions formation of a less stable link between azo-compound and metal with the result that the copper derivative, instead of being co-ordinatively saturated, exhibits weak co-ordinating affinity.

o-Hydroxy-o'-Carboxy-azo-compounds:

The compounds of this type studied were shown to have the simple molecular weight in pyridine, and exhibited co-ordinative unsaturation. They were soluble in aniline or pyridine, forming crystalline derivatives with one molecule of these bases.

o,o'-Dihydroxy-azo-compounds:

This type compound apparently has a monomeric structure in which only one nitrogen of the azo group is co-ordinated, the metal being associated in a 5- and in a 6-membered ring.

Azo-sulfonic acids: (Specifically o-hydroxy-azo-monosulfonic acids)

These form cupric salts at the sulfonic acid groups, the hydroxyls remaining free. These simple copper salts undergo a remarkable change in the presence of alkali or of certain metallic salts, becoming converted into brownish-red complexes in which the copper atoms have the innder type of co-ordination, i.e., are associated with the oxygens of the hydroxyl groups and with azo-nitrogen atoms instead of with the sulfonic groups.

Drew and Landquist, J. Chem. Soc., 292 (1938)

Topic II

STRUCTURE OF CERTAIN COMPLEXES FROM CONDUCTIVITY STUDIES

I. Introduction

Duval, using a slightly modified electrolytic method, examined a great number of solutions of various compounds. Some of the more interesting results follow:

II. Experimental results and proposed structures of various complexes.

The complex formed between $CuCl_2$ and $CdCl_2$ was shown to be entirely $Cu(CdCl_4)$, in the concentration studied, and hot $Cd(CuCl_4)$.

Artificial kainite, usually written $MgSO_4.KCl.3H_2O$, appeared to be a binary electrolyte in water at 25° C. Duval proposed $K[MgClSO_4(H_2O)_3]$ as the formula, where Mg has a co-ordination number of 6. This is apparently a very fragile complex since various tests for cationic Mg are positive.

The Mg in carnallite and schönite likewise migrated to the anode. Structures proposed: for carnallite, $K[MgCl_3(H_2O)_3].3H_2O$; for schönite, $K_2[Mg(SO_4)_2(H_2O)_2].4H_2O$

The double nitrate of cerium and ammonium presumably should be represented by $(NH_4)_2[Ce(NO_3)_6]$.

For the compound between PCl_3 and NH_3, which is a white powder and generally indicated as $PCl_3.6NH_3$, Duval proposes $[P(NH_3)_6]Cl_3$.

Vapor density measurements indicate a bimolecular formula for $FeCl_3$. Electrolytic data support formula $Fe(FeCl_6)$. Among other "auto-complexes" where the metal has the same valence in the cation as it has in the anion Duval arrives at additional formulas as follows: $Co(CoCl_6)$; $Co[Co(CO_3)_3]$; $Mn[Mn(SO_4)_3]$. $AuCl_3$ in concentrated aqueous solution appears to be the auric salt of the acid $HAuCl_4$ - $Au(AuCl_4)_3$; $CoCl_2.2H_2O$ has a triple formula, $Co[CoCl_3(H_2O)_3]_2$.

Among "autocomplexes" in which the metal has a different valence in the cation than it has in the anion are the following: $AuCl_2$ does not exist (Duval), but this is in reality $Au^{I}[Au^{III}Cl_4]$; likewise $Tl^{I}[Tl^{III}Cl_4]$ for $TlCl_2$, and $Tl_3^{I}[Tl^{III}Cl_6]$ for Tl_2Cl_3.

These formulas in the last paragraph above bring out the general principle, first advanced by Abegg and Boländer, that if the same element in two different valence states forms autocomplexes, those are always more stable in which the complex ion contains the element in its most unstable valence state. Thus the compound $Tl^{III}[Tl\ Cl_4]$ has never been prepared (compare with above); cobaltic-cobaltous salts are unknown, whereas cobaltous-cobaltic salts are known and capable of being isolated; Prussian blue is more stable than Turnbull's blue.

Alums, generally considered double salts, may form complexes in solution at certain concentrations. In 0.01 N solution of potash alum all the Al migrates toward the cathode. On the other hand, in concentrated solution, all the Al migrates to the anode, and at intermediate concentrations the Al migrates toward both electrodes

Duval, Bull. soc. chim., 1020 (1938)

R. N. Keller

Inorganic Seminar

November 8, 1938

SULFAMIC ACID: A NEW INDUSTRIAL CHEMICAL

A. Properties of Sulfamic Acid: It is a colorless, odorless, non-hydroscopic, crystalline product which may be handled and packaged commercially in the solid form. It's aqueous solutions are highly ionized, and are practically stable at lower temperatures. Solubilities of its salts are high.

B. Methods of Preparation

C. Inorganic Reactions
1. Reacts with basic oxides, carbonates, and hydroxides giving sulfamate salts. Amphoteric oxides react less readily or not at all.
2. Prevents precipitation of Ag, Hg and Au by alkalies presumably forming salts of the type, $AgNHSO_3Na$ in alkaline solution.
3. Forms complexes with chloroplatinate salts
4. Reacts with chlorine forming N-halogen derivative. Oxidized to H_2SO_4 at higher temperatures by bromine and chlorates.
5. Oxidized by HNO_3 or nitrites but not by CrO_3, $HMnO_4$, or $FeCl_3$.
6. Forms complex with PCl_5

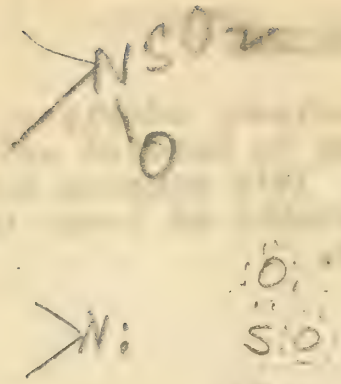
D. Organic Reactions.
1. Reacts with primary alcohols to form ammonium alkyl sulfamates.
2. Alkylation by ordinary procedures yields ester of N-dialkyl sulfamic acids.
3. Aldehydes react with sulfamic acid yielding products which are usually decomposable by water. Products have the structure $RCHOH.NHSO_3M$ or $RCH{=}NSO_3M$.
4. Certain amides react to form the ammonium salt of the sulfonated amide. Complicated side reactions often occur.
5. Phenols and related compounds under certain conditions react with sulfamic acid to give aromatic sulfonated derivatives.
6. Certain unsaturated compounds react to a limited extent with sulfamic acid.
7. Aromatic amine salts may in certain cases b rearranged, first, into ammonium salts of the substituted sulfamic acids and then into the ring sulfonated derivatives of aromatic amines.

E. Potential Applications.
1. Flame proofing agent
2. For applications where a highly ionized acid is desirable or where precipitation of insoluble salts must be avoided.
3. Sulfamic acid shows a definite retarding effect on the precipitation of basic compounds when alkali is added to metal salt solutions.
4. The rearrangement of the aromatic amine salts have useful possibilities in organic synthesis.
5. It should be useful as an anlytical reagent: (1) In acidimetry (2) In determiation of nitrites even in the presence of nitrates.

Reference: Cupery, W. E.: Ind. Eng. Chem. 30, 627-631 (1938)

(other references to literature given with this paper)

H. H. Sisler



PREPARATION AND ANALYSIS OF TRIVALENT OSMIUM

I. Brief discussion of previous work.

II. Preparation of trivalent osmium by electrolysis of K_2OsBr_6 in HBr solution.

A. Preparation of K_2OsBr_6 --
Purified Os $\longrightarrow OsO_4 \longrightarrow H_2OsBr_6 \longrightarrow K_2OsBr_6$

B. Electrolytic cell has carbon anode and platinum gauze cathode, the electrodes being separated by a porous cup.

III. Methods of analysis -- All titrations were potentiometric because of the highly colored solutions and the presence of octovalent osmium in the third method.

A. Oxidation with Br_2 and con. HBr to quadravalent state, removal of excess Br_2 and titration with standard $CrSO_4$.

B. Oxidation to quadravalent state with known excess of Br_2 and con. HBr and titration of unreduced Br_2 with hydrazine sulfate.

C. Oxidation with dilute HBr + Br_2 to octovalent state and titration of ~~liberated~~ unreduced Br_2 with hydrazine sulfate.

IV. Analysis of mixtures of trivalent and quadravalent osmium.
(1) Quadravalent osmium determined by $CrSO_4$ titration, and
(2) a second portion of the mixture is brominated in con. HBr and the total osmium content determined by $CrSO_4$ titration.

V. Determination of constitution of trivalent compound --
Reduced solution evaporated with excess KBr in presence of CO_2 and product analyzed for trivalent osmium after removal of excess KBr.
Molecular weights of 777 and 780 obtained as compared with value of 788 for K_3OsBr_6.

VI. Conclusion -- Trivalent osmium is shown to be present in the electrolyzed solution because (1) the values of the concentrations of reduced osmium agree so well in the three methods of analysis, (2) the amounts of bromine per gram atom agree so closely with the assumed values, and (3) the potential of the reduced osmium solution is so nearly the same as that of the equivalent point in the reduction with $CrSO_4$.
Any one of the three methods of analysis can be used to determine trivalent osmium.

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Loring R. Williams

PRESENT STATUS OF POTASH

I. Historical

The Permian Salt Basin of Texas, New Mexico, Colorado, Oklahoma, and Kansas has interested geologists since about 1852 and has for some time been considered a probable source for potash minerals. Drilling operations by the Geological Survey were begun in 1910 in a search for oil, gas, and potash. Potash material was first discovered in 1912, sylvite in 1925. The Searles Lake region was probably first visited by white men in 1849 by some "forty-niners" seeking a short cut to the gold fields. It was named for John Searles who operated a borax extraction plant there from 1878-1895. Presence of potash material was confirmed in 1912 and in 1914 a plant for its recovery was erected.

II. Geology of the Potash Deposits.

The salts of the Permian Basin are believed to be of oceanic origin, deposited by an ocean which gradually receded southward during that period. Some of the potash was deposited by desiccation and some by replacement after deposition. The deposition was not uniform for several reasons. In the Searles Lake region final deposition laid down a spongelike mass of salt with saturated brines filling the openings.

III. Mining

At Carlsbad, at present the main source of potash materials in the Permian Basin, the sylvinite bed is in general horizontal. A three compartment shaft was sunk to the mineral layer and mining carried out by the room and pillar method similar to that employed in modern coal mines. The ratio of ore extracted to that left in the pillars is roughly 60 to 40 with some further recovery of the latter indicated. At Searles Lake the saturated brine is simply pumped into the refinery.

IV. Refining

The chemistry involved in the case of the New Mexico sylvinite is fairly simple; it is essentially a separation of Na and K chlorides. This is facilitated by the fact that the NaCl saturation curve is actually reversed in a solution saturated with KCl. The chemistry of the Searles Lake brine is complex. Phase rule studies on various portions of the total system have shown that evaporation at 20° C. will not separate the Na and K salts. Evaporation at high temperature causes precipitation of Na salts only, after which rapid cooling allows crystallization of the KCl alone. The borax is maintained in saturated solution.

V. Uses

Potassium is one of 14 elements shown to be essential to plant growth and consequently the use of fertilizers containing potash has grown steadily. When soluble potash enters the soil it quickly dissolves in the soil solution. Some is immediately absorbed by plants but most of it undergoes a base exchange reaction with material in the soil and in this form is readily available to plants. Some of this eventually passes over into a non-exchangeable form. Potassium does not enter into any permanent organic combination in plants; in fact is may be completely leached out of plant tissues. Among other things, potassium seems to have a definite effect upon water, nitrogen, and carbon dioxide assimilation and retention. Plants of higher potassium content seem able to utilize the energy of sunlight to a

greater degree. Potassium salts of chemical grade are finding constantly increasing use in soap manufacture, dyes, explosives, and glass manufacture. The last named is a large user of high grade K_2CO_3 and KNO_3 sinc potassium gives some highly desirable qualities to glass.

VI. Isotopes and Radioactivity

By means of a modified Geiger counter with a low background count it has been shown that only beta and gamma rays can be detected from radioactive potassium, the ratio being close to 100 to 1. The number and energy of the rays can be measured. It can be shown that K^{40} is the radioactive isotope. It has a half life of close to 1.2 billion years. The relative abundance of the K^{39}, K^{40}, and K^{41} isotopes, the only three known, is 8300, 1, and 585, respectively. Either Ca or A may be formed by the disintegrating K^{40}. The ratio K^{39}/K^{41} may be measured by means of the mass spectrograph and the atomic weight calculated, provided the value for the packing fraction is known. Abundance ratio and atomic weight determinations made by this method on K from a number of different sources showed some slight variation.

Reference:

Ind. and Eng. Chem. 30 853-896 (1938)

Paul F. Cundy

THE CARBONYL HYDRIDES OF IRON AND COBALT

The carbonyl hydrides were first noticed in the reactions of certain carbonyl complexes with acids and the reaction of the metallic carbonyls with bases. The only ones which have been prepared have been $Fe(CO)_4H_2$ and $Co(CO)_4H$.

Iron carbonyl hydride, $Fe(CO_4)H_2$ has been prepared in the following two types of reactions:

1.a) $Fe_2(CO)_4en_3 + 8H^+ \rightarrow Fe(CO)_4H_2 + Fe^{++} + 3(en2H)^{++}$

b) $3Fe(CO)_3 + 2H^+ \rightarrow Fe(CO)_4H_2 + Fe(CO)_5 + Fe^{++}$

or $2Fe(CO)_3 + 2H^+ \rightarrow Fe(CO)_4H_2 + Fe^{++} + 2CO$

2.a) $Fe(CO)_5 + 2OH^- \rightarrow Fe(CO)_4H_2 + CO_3^{--}$

b) $Fe(CO)_5 + NaOR + H_2O \rightarrow Fe(CO)_4H_2 + ROCOONa$

Cobalt carbonyl hydride has been prepared in these same two ways as well as an additional way:

1.a) $2Co(CO)_3M + 2H^+ \rightarrow Co^{++} + Co(CO)_4H + 2CO + 1/2\ H_2 + 2M$

b) $Co_2(CO)_5M + 2H^+ \rightarrow Co^{++} + Co(CO)_4H + CO + 1/2H_2 + M$

2.a) $3Co(CO)_4 + 2OH^-$ (strong base) $\rightarrow 2HCo(CO)_4 + Co(CO_3)$ (polymer) $+ CO_3^{--}$

b) $3\ Co(CO)_4 + 2H_2O$(weak base) $\rightarrow 2HCo(CO)_4 + Co(CO)_4 + Co(OH)_2 + 4\ CO$

3.a) $2CoCl_2 + 12KOH + 11CO \rightarrow 2KCo(CO)_4 + 3K_2CO_3 + 4KCl + 6H_2O$
use cysteine or tartrate to form intermediates

b) $6CoCl_2 + 12KSCSOC_2H_5 + 5CO + M \rightarrow Co_2(CO_5)M + 4Co(Xa)_3$

Then same as 1b.

Iron carbonyl hydride melts at -70° C, and decomposes at -10°C. Decomposition proceeds as follows:

$$Fe(CO)_4H_2 \rightarrow Fe(CO)_4 + H_2$$

Dry hydrogen chloride and iodide have no effect at -30°.

Excess of iodine at -80°: $Fe(CO)_4H_2 + 2I_2 \rightarrow Fe(CO)_4I_2 + 2HI$
in samall amounts: $Fe(CO)_4H_2 + I_2 \rightarrow Fe(CO)_4I_2 + H_2$

Air oxidizes $Fe(CO)_4H_2$ to $Fe(CO)_4$ readily. Neutral or acid solutions are not stable in the absence of air, but are stabilized by alkali.

Salts of the type $[Fe(CO)_4H]_2\ [Co(NH_3)_6]$ and $Fe(CO)_4\ Hg$ have been prepared. They are stable in the absence of air and water.

Cobalt carbonyl hydride melts at -26.2° C and decomposes at -18° C. $2Co(CO)_4H \rightarrow 2Co(CO)_4 + H_2$. Salts of the hydride have been prepared.

Both hydrides are volatile and can be distilled in a higer vacuum or in a stream of carbon monoxide.

There has been disagreement about whether the carbonyl hydri hydrides are acids. The results seem to show that the carbonyl hydrides are weak acids - on the order of carbonic acid and acetic acid.

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Eugene O. Brimm

E

THE SULFUR INDUSTRY, HISTORY AND DEVELOPMENT

I. Historical.

Very early literature tells us that sulfur has been in general use at all times. Sulfur mining was officially recognized in Italy as early as the year 1000. Conditions of sulfur mining in Italy in the 19th century were in a chaotic state. The invention of the MacDougal pyrites burner in 1870 and the development of sulfur recovery from the residues of the Le Blanc soda process by the Chance-Claus method further complicated the situation. More economical production through installation of Gill furnaces coupled with more modern mining methods have improved conditions in Europe.

II. Developments in America.

First recorded production of sulfur was in Mexico shortly after 1519. Sulfur was discovered in Louisiana in 1865. Numerous attempts to mine this deposit were unsuccessful until the work of Frash which started in 1890.

III. Geology and Formation of Sulfur Deposits.

Sulfur occurs in many localities as the result of volcanic action. The deposits in Texas and Louisiana occur in large salt domes. The most probable explanation for its occurrence is the reduction of sulfur compounds and their subsequent oxidation to free sulfur.

IV. World Developments Since 1900.

American and European operators worked to stabilize production. Improved methods of mining together with the increased use of sulfur caused great expansion in the production of sulfur.

V. Technical Improvements.

Technical improvments have resulted in increased economy of operation. Water softening difficulties incident with the extreme temperatures used have been overcome. Sulfur transporation and storage have been bettered. Probably the most difficult problem, bleed water treatment to prevent pollution and utilize its heat, has been solved to a large extent.

References:

J. Ind. Eng. Chem. 30, 740-58 (1938)

Herrick Henry

HYDRIDES AND DEUTERIDES OF THE ALKALI METALS

Hydrides:

First systemmatic study was made by Moissan in 1902-04;
- Prepared hydrides of sodium, potassium, rubidium, and cesium by passing hydrogen over the hot metal.
- Encountered difficulties due to action of metals on glass.
- Hydrides prepared were white, needle-like crystals; saltlike; insoluble in CCl_4, CS_2, C_6H_6, and ether.
- Hydrides were very unstable and thus excellent reducing agents, Burned in oxygen, fluorine, chllrine, and moist air.
- By Analysis, formulas shown to be NaH, KH, RbH, and CsH.

Newer methods of preparation avoid effect on glass;
- Hydrides sublimed from steel reaction tube into glass vessel.
- Hydrogen made to diffuse through closed nickel cylinder and react with alkali metals there.
- Activiated hydrogen passed over metals at room temperatures.
- Electric discharge passed through hydrogen at low pressure in container with walls coated with alkali metal.

Additional properties;
- Hydrides crystallize in NaCl type crystal.
- When fused and electrolyzed, evolve hydrogen at anode.
- Decomposition pressure increases with temperature so that a straight line is produced by graphing log p against 1/T.

Possible uses
- Fused LiH as solvent for electrolysis.
- Hydrides as sensitive elements in photoelectric cells.
- Catalysis of organic hydrogenation reactions.
- Convenient, portable source of hydrogen (LiH).

Deuterides:

Preparation of NaD and KD by Hackspill and Borocco;
- Used Moissan's method
- Stated rate of combination of deuterium with alkali metals to be slower than that of hydrogen.

Study by Sollers and Crenshaw of NaD, KD, NaH, and KH;
- Dissociation pressures approximately double, those of the corresponding hydrides at the same temperature.
- Possible separation of hydrogen isotopes on basis of respective reactions with potassium.

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J. B. Work

February 14, 1939 Inorganic Seminar

"FREEZING"

Theories

1) Kornfeld's, who postulated that freezing was determined by probability.

2) Tammann and Othermer, who postulated the presence of "memory" crystals i.e., even though the liquid may be well above its melting temperature, some frew crystals remain which may serve as nuclei for further crystallization of the freezing point.

3) Herzfeld's. Presence of any impurities, such as dust particles etc. called motes, which may serve as nuclei for the formation of crystals. a) Modification of Hinshelwood and Hartley. Motes act as catalysts in crystallization.

4) W.T. Richard's. Combination of (2) and (3). Crystals remain but are absorbed by motes.

Spontaneous freezing point.

As the temperature of a liquid is gradually lowered a point is reached at which a new phase (ice) appears. It was found that each specimen had a characteristic temperature below 0°C. at which it froze spontaneously. Although this temperature was fairly permanent over short periods of time it was never permanent over long periods. It was shown that there were four main types of deviation.

a) First few freezings discordant with later fairly constant freezings

b) Over a period of weeks the spontaneous freezing point slowly changes, usually decreasing.

c) There may be an abrupt change which is relatively permanent

d) It may be quite erratic over long periods of time.

The spontaneous freezing point depends on the source of the water, or, in other words, on the purity.

Effect of heating.

In general, the extent to which a liquid may be supercooled, increases with preliminary heating. The controlling factor seems to be the temperature to which the melt is heated and not the length of time of heating.

Effect of motes.

The size and not the number of motes was shown to effect the freezing point, by mixing a sample having a spontaneous freezing point of -19° C. and one having a spontaneous freezing point of -7°C., in the ratio of 9 to 1 respectively. The resulting mixture froze at -7°

Sedimentation.

Some water which initially forze at -12.2°C., was allowed to stand very quietly for two weeks, after which samples were very carefully drawn from both the top and bottom layers. The top layer forze at -12.8°C. and the bottom at -7.6°C. initially, but slowly decreased in four days to -12.1°C.

Agitation and volumes.

It was found that relatively large volumes of water with a spontaneous freezping pount of -15° C. could be shaken and sloshed about -14°C. without resulting crystallization.

Types of freezing. If water is cooled rapidly, crystallization takes place rather slowly from the walls of the vessel inward, while if cooled slowly, crystallization is quite rapid. The fewer the nuclei responsible for freezing the clearer seems to be the resulting ice. Approximately a single nuclei is present if a seed crystal is used. In this case freezing takes place slowly from the crystal outward, resulting in very clear transparent ice.

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Thomas O'Brien

Inorganic Seminar

February 20, 1939

Inorganic Materials in the Study of Chemiluminescence

I. Introduction

A. Definition of terms

Chemiluminescence is light which appears as a direct result of chemical action.[1] This discussion, however, will be limited to those forms of chemiluminescence which are produced as a result of low temperature oxidations in the liquid or solid phase.

B. Background

1. Bioluminescence (fireflies, fish, etc) first form to be studied.
2. Artificial chemiluminescense of similar type was early observed. (pyrogallol, lophine, etc.)
3. Systematic studies of relationship between molecular or atomic structure and chemiluminescence is still in its infancy.

II. Types and examples

A. Inorganic chemiluminescence

1. $P + O_2$
2. $Na + Air$ [2,3]

Woodrow and Bowie[2] showed that this reaction was due to the water vapor in the air since it did not take place in dry air.

3. Galvaniluminescence (production of luminescence during electrolysis. For example, light is produced at the anode in the electrolysis of a $NaHCO_3$ solution using an aluminum anode.[4]
4. Oxidation of $Si_6O_3H_6$ with $KMnO_4$.[1]

B. Organic

1. Luminol[5] (3 aminophthalhydrazide) (various oxidizing agents)

This substance produces the brightest Chemiluminescence so far discovered.

2. Lophine[6] (triphenylglyoxaline) (various oxidizing agents)
3. Bioluminescence. (The oxidation of luciferin by air in the presence of the enzyme luciferase.)
4. Aromatic grignard reagents[7] (The brightest one reported is p-chlorophenyl-magnesium bromide.)
5. Flavylium salts[8] (This reaction, discovered by the speaker in this laboratory, should be of interest to inorganic chemists because of the electrovalent salt like structure. This structure seems to be essential to the luminescene of this type of compound)

I. Conditions for luminescent oxidation.

A. Basic solution[12]

B. Suitable solvent (alchohol, acetone etc. for organic compund

C. Oxidizing agents.

1. A few reactions will luminesce with a singel oxidizing agent. For example:
   a. O_2 or air with grignard.[7]
   b. O_3 with various dyes.[9]

c. H_2O, N_2O, or NO_2 or Na[8,10]
D/ O_2 + sound waves on luminol[11]
e. Chloropicrin (CCl_3NO_2) or grignard reagents.[1]
f. H_2O_2 or NaClO etc singly on luminol or lophine gives a weak luminescence.

2. Most luminescent reactions require another oxidizing agent.[12] Many examples are known of each type. Unless otherwise noted all of the following oxidizing agents have been used with luminol.
   a. Peroxides
      1. H_2O_2 (most commone)
      2. Na_2O_2
      3. BaO_2
      4. Sodium perborate $NaBO_3$ (Useful because it is a stable non deliquescent solid.)
   b. Other oxidizing agents.
      1. $K_3Fe(CN)_6$
      2. NaCLO most common
      3. Cl_2 or Br_2 ___ HCLO or HBrO
      4. KIO_4
      5. $K_2S_2O_8$
      6. Bismuthis acid $HBiO_3$
      7. Permolybdic acid
      8. Pertungstic acid
      9. Pervanadic acid
      10. Pertitanic acid
      11. Perchromic acid(ether extract)
      12. Perceric compound
      13. $KMnO_4$ (very poor light may be due to brightly colored solution.)
      14. OsO_4 (with dimethyl-bicridylium salts.)[13]

Method of prep.
$BiO(OH)+H_2O_2$ acid
NH_4 molybdate$+H_2O_2$
$Na_2WO_4+H_2O_2$ acid
$VOCl_3+H_2O_2$ acid
$TiCl_3+H_2O_2$ acid
$K_2Cr_2O_7+H_2O_2$ acid
$Ce_2(So_4)_3+H_2O_2$ Basic

3. The following exidizing agents gave not light when used with H_2O_2 or lophine: Fe, Cu, MnO_2, Ag_2O, PbO_2, $NaBrO_3$ KCl_3, KIO_3, $NaClo_4$, K_2CrO_4, $Hg(NO_3)_2$, $Cu(NO_3)_2$, $LeCl_3$, $Le(OH)_3$.

IV. Possible theory to explain the use of certain oxidizing agents[12]

It will be noted that the oxidizing agents listed above have the property of reacting with hydrogen peroxide in basic solution to give free oxygen. It is suggested that oxygen produced by this method is at the instant of formation in just the right state to oxidize the organic molecules with the production of light, while oxygen gas or oxygen liberated by the catalytic decompostition of hydrogen peroxide is not in the right state. Much additional work is needed to prove or disprove this theory.

V. Demonstration of Chemiluminescence.
   A. Luminol + NaClO + H_2O_2
   B. Luminol + $K_3Fe(CN)_6$ + H_2O_2
   C.. "Chemglo" +
   D. 3-methoxy -4-bromoplavylum chloride + NaClO +H_2O_2
   E. " Drops of liguid fire."

+"Chemglo" is a commercial product produced by Evans W. Cottman, Madison, Indiana.

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Bruce Moffett

Inorganic Seminar February 28, 1939

BORON HYDRIDES

HISTORY

1. Davy in 1809 first observed a gas which burned with a blue-green flame and had a disagreeable odor, mixed with the H_2 formed by the action of water on the mass obtained from B_2O_3 and K.
2. Jones and Taylor about 1880 obtained a mixture of boron hydrides by the action of HCl on magnesium boride.
3. Stock, Wiberg, and collaborators (since 1912) separated the hydrides and have studied them in great detail.
4. Sidgewick in 1927 proposed structures with single electron bonds.
5. Schlesinger and Burg (1931) improved the method of preparing these compounds and have studied them since.
6. Bauer in recent years has made electron diffraction studies of the hydrides and derivatives.
7. The main reason for interest in the boron hydrides is the problem of what structures they can have, since the usual valence relationships evidently do not hold; their preparation and study are difficult, requiring vacuum apparatus and low temperatures.

PREPARATION

1. Stock's method: long action of HCl on magnesium boride (6 ml. obtained from 2 kg. boride) fractionated in vacuum apparatus: at -30° $B_{10}H_{14}$ (solid) and B_6H_{10}, at -95° B_5H_9, at -120° B_4H_{10} (m.p. -18°). B_4H_{10} heated in a closed tube at 90° forms B_2H_6 (b.p. -80°). Later improvements: Be boride better than Mg boride because no Si hydrides are obtained. Al boride and Ce boride have also been used. H_3PO_4 gives better yields than HCl.
2. Schlesinger and Burg method: BCl_3 and H_2 in an electric arc at reduced pressure form B_2H_5Cl, from which B_2H_6 is obtained (100 ml. or more per hour). B_2H_6 forms B_5H_9 at 120-130°.
3. Stock (new high vacuum apparatus): preparation of other hydrides from B_2H_6. At 180° and 0.2-0.6 mm. B_5H_{11} (m.p. -123°) is formed, with some B_4H_{10}; these are separated by fractional condensation. B_5H_{11} and H_2 form B_4H_{10}. B_2H_6 at 250° and 120 mm. forms B_5H_9 and B_5H_{11}, which are fractionated. B_6H_{10} must still be prepared from acid and boride. BBr_3 was found to have several advantages over BCl_3 for the preparation of B_2H_6.
4. BH_3 is not known. Its transitory existence in the decomposition of BH_3CO to B_2H_6 and CO has been postulated to explain the varying rate of the reaction.
5. Band spectra due to the molecule BH have been observed.

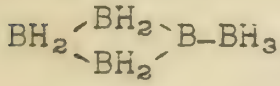
REACTIONS

1. With oxygen. Most of the hydrides are spontaneously inflammable in air. Some react explosively.
2. With water. All the hydrides are hydrolyzed by traces of moisture; boric acid is formed.
3. With ammonia. Salts (non-volatile white solids) are formed: $B_2H_6(NH_3)_2$, $B_4H_{10}(NH_3)_4$, $B_5H_9(NH_3)_4$. The latter two of these are chlorinated in steps by HCl, Cl replacing H attached to B. The first two when heated form the six-membered ring compound $B_3N_3H_6$, and when they are electrolyzed in liquid ammonia solution NH_4 is obtained at the cathode and B_2H_4 and B_4H_6 at the anode, H_2 being evolved and the anions adding NH_2 groups.

4. With metals. B_2H_6 reacts with amalgams of Na, K, and Ca, the metals being added, and no hydrogen evolved. B_4H_{10} similarly adds 2Na or 2K. B_5H_9 adds 2K.
5. With HCl or HBr. B_2H_6 and B_4H_{10} react with HCl or HBr to form B_2H_5X and B_4H_9X. B_5H_9 and $B_{10}H_{14}$ do not react.

STRUCTURE

1. There are insufficient electrons in the boron hydride molecules for normal bonds (electron pairs).
2. Hellriegel suggested an attractive force due to the inner shell - the two K electrons of the boron atom.
3. Wiberg advanced structures with double bonds: $(H_2B{=}BH_2)H_2$, e.g. Evidence adduced: NH_4 salt formation shows acid character: replacement of H by halogen shows non-acid H; addition of metals shows unsaturated nature; parachor of B_2H_6, calculated for unsaturated structure, agrees with experimental value from surface tension.
4. Sidgewick proposed the single electron bond: 2H attached thus in B_2H_6, 4 in B_4H_{10}, etc.
5. Pauling agreed with this, considering that such bonds can be formed when there are two possible electronic states with essentially the same energy, differing only in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired electron attached to the second atom.
6. Mullikan suggested that in each BH_3 group the three H atoms are bound by 5 electrons (2s and 3p) shared equally by the three.
7. Bauer compared electron diffraction results with theoretically calculated curves for possible structures. He found the B_2H_6 curve very similar to that for ethane, but quite different from that for ethylene or for Wiberg's structure. A similar study of B_4H_{10} showed it to have a structure like that of butane. B_5H_9, however, appears to have a four-membered ring structure:



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Arthur E. Kott

ULTRASONIC REACTIONS

Ultrasonic waves are those sound waves having frequencies above the audible range, i. e., above 17000 cycles per second. They are commonly produced by taking advantage of the piezo-electric property of quartz or tourmaline crystals. Mechanical oscillations are stimulated in the crystal by placing it in an alternating electrical field. The vibrating system is immersed in a bath of transformer-oil and the mixtures to be investigated are placed in thin walled glass tubes which are clamped in the oil bath.

Some effects which have been observed are the following:

1) Small concentrations of H_2O_2 have been found in water saturated with O_2. When water is saturated with air, H_2O_2 and HNO_2 are found after treatment with ultrasonic waves.

2) Examples of intensive ultrasound action on passivity and activation processes include the lessened passivity of Fe in H_2SO_4, Pb in Na_2CO_3, Fe and Cr in conc. HNO_3, and hastened anodic passivity of Al and of Ni in weakly acidic H_2SO_4 solution.

3) Ultrasound waves certain reactions including the hydrolysis of dimethyl sulphate, the evolution of CO_2 by the action of H_2SO_4 or HCl on marble, and the liberation of H_2 from H_2SO_4 or HCl by Zn.

4) The molecular rearrangement of benzazide ($PhCON_3 \rightarrow N_2 + PhNCO$) is induced by ultrasonic waves.

5) Solids of low cohesion, e.g., mica, talc, gypsum, graphite, sulphur, and hematite may be dispersed in liquids by ultrasonic waves. Solid metals have not been so dispersed. However, when a plate of an electro negative metal is dipped with an aqueous solution of a metallic salt and supersonic waves are applied, the colloid of the depositing metal is obtained.

6) Detonation of NCl_3 and NI_3

7) Boiling point lowerings amounting to two degrees were found by treating CCl_4, $PhCH_3$, Et_2O, and H_2O with ultra-sound. The transition point of yellow HgI_2 to the red modification is lowered through ultrasound.

8) Depolymerization is effected by ultrasonic waves.

9) Ultrasonic waves may bring about formation of emulsions and fogs, or they may cause coagulation of a colloid.

No exact explantion as to the mechanism of reactions influenced by ultrasound has been attempted. There is, however, general agreement among theorists that cavitation phenomena resulting from the action of ultrasonic waves are in some way responsible for the effects produced. Cavitation refers to the formation and subsequent collapse of minute gas bubbles in a liquid which is subjected to a disrupting force. The collapse of these hollow spaces can bring about large ratios of energy concentration as it has been calculated that pressures of thousands of atmospheres may be developed at the moment when a cavity collapses to a small fraction of its original diameter. High kinetic energies are thus concentrated in very small regions.

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Betty Rapp

Inorganic Seminar March 14, 1939

Organogermanium Compounds

I. History

In 1871 Mendeleeff predicted that ekasilicon (germanium) would form volatile organometallic compounds.
Prediction verified by Winkler in 1886.
After nearly forty years of neglect, contributions to the field have recently been made by Morgan, Dennis, Kraus, Schwarz and others.

II. Hydrides of Germanium.

A. Preparation

1. $Mg_2Ge + NH_4Br \xrightarrow{\text{liquid } NH_3} GeH_4$ + higher hydrides
2. $CaGe_2 + HCl \longrightarrow (GeH_2)_x$
3. $NaGe + HCl \longrightarrow (GeH)_x$

B. Properties

1. GeH_4 - colorless gas, stable under ordinary conditions
   $GeH_4 + HCl \longrightarrow GeH_3Cl + GeH_2Cl_2$
   $GeH_4 + Na \longrightarrow GeH_3Na + H_2$
2. $(GeH_2)x$ - amorphous, yellow powder, stable when dry
   $GeH_2 + O_2 \longrightarrow Ge(OH)_2$ (explosively)
   $GeH_2 + NaOH \longrightarrow Na_2GeO_2$
   $GeH_2 + HCl \longrightarrow GeCl_2 + GeH_4 + Ge_2H_6 + \ldots\ldots + H_2$
3. $(GeH)x$ - dark brown powder, very unstable when dried in air
   $GeH + HNO_3 \longrightarrow GeO_2$
   $GeH + X_2 \longrightarrow GeX_4$
   $GeH + HCl$ (dry) $\longrightarrow$ no effect below decomposition temp.

III. Substituted Germanes

A. Simple - R_4Ge

1. Preparation
   a. $RMgBr + GeCl_4 \longrightarrow R_4Ge$ (low yields)
   b. $R_2Zn + GeCl_4 \longrightarrow R_4Ge$ (high yields)
   c. $R_3GeBr + R'Br + Na \longrightarrow R_3GeR'$
2. Properties
   White solids if R is aromatic; colorless liquids if R is aliphatic
   $R_4Ge + Br_2 \longrightarrow R_3GeBr + R_2GeBr_2$
   $R_4Ge + Na \longrightarrow R_3GeNa + R_2GeNa_2$

B. Mixed Germanes - $R_{4-n}GeXn$

1. $(R_3Ge)_2O + HX \longrightarrow R_3GeX$
2. $R_2GeO + HX \longrightarrow R_2GeX_2$
3. $RI + GeI_2 \longrightarrow RGeI_3$
4. $CsGeCl_3 + RI \longrightarrow RGeCl_3$
5. $R_3GeX + H_2O \longrightarrow (R_3Ge)_2O$
6. $R_2GeX_2 + H_2O \longrightarrow R_2GeO$
7. $RGeX_3 + H_2O \longrightarrow (RGeO)_2O$
8. $R_3GeBr + KNH_2 \longrightarrow R_3GeNH_2$
9. $R_3GeBr + NH_3$ (liquid) $\longrightarrow (R_3Ge)_3N$
10. $R_3GeNa + NH_4Br \longrightarrow R_3GeH$
11. $(R_3Ge)_2 + Na \longrightarrow R_3GeNa \xrightarrow{O_2} R_3GeONa \xrightarrow{NH_4Br} R_3GeOH$
12. $R_3GeNa \xrightarrow{D.C.} R_3GeH + (R_3Ge)_2 + N_2 + Na$

    Comparison of substituted germanes with analogous organometallic compounds of the fourth group.

C. Miscellaneous

1. $R_2GeCl_2 + Na \longrightarrow R_2Ge \xrightarrow{Na} R_2GeNa_2$
2. $R_3GeBr + Na \longrightarrow (R_3Ge)_2$
3. $R_3GeNa + R_2GeCl_2 \longrightarrow R_8Ge_3$
4. $C_6H_5GeCl_3 + K \longrightarrow (C_6H_5Ge)_6$ - probably an open chain structure

5. $R_3GeBr + Na_2S \rightarrow (R_3Ge)_2S$

IV. Applications

No important applications have been found as yet. Attempts to use some of these compounds in chemotherapy have met with discouraging results.

F. Grosser

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Inorganic Seminar March 21, 1939

The Determination of Molecular and Ion Weights by Dialysis

I. Development of the Method

Diffusion through a membrane proceeds according to the equation $C_t = C_o e^{-\lambda t}$ where C_o and C_t are the initial and final concentrations, respectively, e is the base of the natural logarithms, and λ is a coefficient dependent on the membrane, the specific surface, the concentration, the presence of other diffusible and non-diffusible substances, and the temperature. It is called the dialysis coefficient.

The dialysis coefficient remains practically constant during dialysis of a homogeneous substance, becomes smaller during dialysis of a non-homogeneous substance. This indicates a relation between it and the molecular weight of the substance dialyzed. This relation, in diffusion experiments (without a membrane) is $D\sqrt{\text{molecular weight}} = K$ or $D_1\sqrt{M.W._1} = D_2\sqrt{M.W._2}$ where D is the diffusion coefficient. Under proper conditions the same relations are shown to hold for dialysis, substituting λ for D. The latter method has many advantages over the former. Solutions to be dialyzed are kept as dilute as accurate analysis for C_o and C_t will permit. Foreign substances in moderate concentration have no effect and an electrolyte which will not react with the dialyzing material is necessary in ion weight determinations to allow free diffusion of individual ions. The method generally used was comparison of the unknown with a reference ion, generally $S_2O_3^{--}$, CrO_4^{--}, or in acid solution $Fe(CN)_6^{---}$, though good results were obtained using many other reference ions.

II. Apparatus and Procedure

The apparatus is essentially a thermostat (5-6 liter capacity) above which is suspended a small dialyzer cell fitted with a stirrer.

A typical run involves dialyzing a solution of 35 cc. of the material being studied into 45 liters of a solution, also used as the solvent in the dialyzer, through a very permeable membrane (cuprophane). Runs of 1/2, 1, and 1 1/2 hours are usually made. The dialysis coefficient is determined for the unknown and reference ion solutions and molecular or ion weights determined therefrom.

III. Results

Determinations have been carried out on a vast number of compounds of many different types. The attempt below at classification is not clear cut. Only a few typical examples are shown in each case.

A. Ion hydration

Some confusion here as to hydration of reference ion.

State that water bound as aquo complex and as water of hydration in solution may be found. e.g. $[Fe(H_2O)_{18}]^{+++}$ $41H_2O$

B. Simple Anionic complexes

1. Weak acids of amphoteric bases $[Sb(OH)_6]^-$ $[Zn_2(OH)_8]^{-4}$
2. Aquo phosphate and arsenate ions at varying p^H
3. Oxalato compounds $[FeOx_3]^{-3}$ $[Fe_2Ox_4]^{-4}$
4. Thiocyanate complexes
5. This anions
6. Uranyl acetate complex

C. Cation complexes

Used various Co and Cr ammines and substituted ammines. Found $[Coen_3]^{+3}$ and $[Copn_3]^{+3}$ dimeric

D. Complexes whose central ion is complex

Certain complex cations and anions may combine to form still more complex ions.

It has been shown that cations of the general type $[Cr(NH_3)_6]^{3+}$ will combine with 4 moles of sulfate, selenate, mono hydrogen phosphate or arsenate, oxalate, malonate, succinate, or citrate to form a "complex" complex anion which migrates to the anode on electrolysis. This same type of cation may also serve as the central ion for 4 ferrocyanide ions yielding an anion.

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5.	" and Eckardt	ibid	224	93	(1935)
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7.	" " "	ibid	224	283	(1935)
8.	" " "	ibid	225	33	(1935)
9.	" " "	ibid	225	221	(1935)
10.	" " "	ibid	225	312	(1935)
11.	" " "	ibid	225	365	(1935)
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Paul F. Cundy

Inorganic Seminar March 31, 1939

RUTHENIUM AMINES

Compound	Color and crystals	solubility	remarks
Ru^{++} Tetrammines			
$[Ru(NH_3)_4(SO_2)Cl]Cl$	red-brown needles	sl.s	
$[Ru(NH_3)_4(SO_2)H_2O](NO_3)_2$	yellow needles		liberates HNO_3 on dissoc.
$[Ru(NH_3)_4(SO_2)H_2O]S_2O_6$	pearly yellow	sl.s	H_2O tightly held
Ru^{++} Pentammines			
$[Ru(NH_3)_5SO_3].2H_2O$	colorless plates	v.s	
$[Ru(NH_3)_5SO_2]S_2O_6$	long red needles	sl.s	
$[Ru(NH_3)_5SO_2]SO_4.2H_2O$	red prisms	s.	loses $4H_2O$ easily
Ru^{++} Luteo Salts			
$[Ru(NH_3)_6]_2(SO_4)_3.5H_2O$	colorless	s.hot	loses $4H_2O$ at 100°
$[Ru(NH_3)_6]Cl_3$	light yellow	v.s.	
$[Ru(NH_3)_6](NO_3)_3.HNO_3$	white 1 cm. needles	i. conc. HNO_3	quite solu 100% HNO_3
Ru^{+++} Purpureo Salts			
$[Ru(NH_3)_5Cl]Cl_2$	yellow heavy ppt.	sl.s	
$[Ru(NH_3)_5Cl]SO_4.2H_2O$	yellow needles		lose H_2O even in (damp air
$[Ru(NH_3)_5Cl]S_2O_6$	yellow needles	i.cold	
Ru^{+++} Roseo Salts			
$[Ru(NH_3)_5OH]S_2O_6$	small colorless	i.	
$[Ru(NH_3)_5H_2O](NO_3)_3$	square leaves	i.dil.HNO_3	
$[Ru(NH_3)_5H_2O]_2(S_2O_6)_3.2H_2O$	colorless plates	s.	very stable
Ru^{+++} Praseo Salts			
$[Ru(NH_3)_4Cl_2]Cl.H_2O$	long orange prisms	s.	loses H_2O easily
$[Ru(NH_3)_4Cl_2]ICl_2$	light brown	i.	
$[Ru(NH_3)_4Cl_2]_2S_2O_6$	orange-yellow	i.	
Ru^{+++} Violeo Salts			
$[Ru(NH_3)_4Cl_2]Cl.3/4H_2O$	orange needles	s.	$2/3H_2O$ very tightly held
$[Ru(NH_3)_4Cl_2]SO_4.H_2O$	flat orange prisms	sl.s.	
$[Ru(NH_3)_4Cl_2]_2S_2O_6$	yellow prisms	sl.s	

Preparation of starting material for each series.

1. Luteo salts

$RuCl_3 + 6NH_3 \rightarrow [Ru(NH_3)_6]Cl_3 \rightarrow [Ru(NH_3)_6]_2(SO_4)_3.5H_2O$

2. Purpureo salts

$[Ru(NH_3)_6]_2(SO_4)_3.5H_2O \rightarrow [Ru(NH_3)_5Cl]Cl_2$

3. Roseo salts

$[Ru(NH_3)_5Cl]Cl_2 \rightarrow [Ru(NH_3)_5OH]Cl_2$

$[Ru(NH_3)_5OH]^{++} + H_2O \rightleftarrows [Ru(NH_3)_5H_2O]^{+++} + OH^-$

4. Praseo salts

$[Ru(NH_3)_5Cl]Cl \rightarrow [Ru(NH_3)_4(SO_3H)_2]$

$[Ru(NH_3)_4(SO_2)Cl]Cl \rightarrow [Ru(NH_3)_4Cl_2]ICl_2 \rightarrow [Ru(NH_3)_4Cl_2]Cl.H_2O$

5. Violeo salts

$[Ru(NH_3)_5OH]S_2O_6 \rightarrow [Ru(NH_3)_4C_2O_4]_2S_2O_6 \rightarrow$

$[Ru(NH_3)_4Cl_2]Cl \rightarrow [Ru(NH_3)_4Cl_2]Cl.3/4H_2O$

6. Sulfito tetrammines of Ru^{++}

$[Ru(NH_3)_5Cl]Cl_2 \rightarrow [Ru(NH_3)_4(SO_3H)_2] \rightarrow [Ru(NH_3)_4(SO_2)Cl]Cl$

7. Sulfito pentammines of Ru^{++}

$[Ru(NH_3)_4(SO_2)Cl]Cl \rightarrow [Ru(NH_3)_5SO_3].2H_2O$

Properties

Ru^{+++} forms stable ammines with coordination number 6. These ammine salts bear striking resemblances to Co and Cr ammines in crystal form, stability, composition, quantity and stability of water of crystallization, and in formation of mixed salts.

All Ru^{++} ammines so far prepared are diamagnetic; all Ru^{+++} ammines are paramagnetic with a magnetic moment of about 2 Bohr magnetous.

The sulfito ammines and the violeo dibromides listed in the table are the first that have been prepared with any metal.

The Ru^{+++} ammines are lighter in color than the corresponding Co, Cr salts. The Ru^{+++} chlorides are lighter than the bromides and the series have the following order of increasing color in strict analogy to the Co, Cr salts: luteo, purpureo, praseo, violeo →

Comparison of pentammine series of Cr, Co, Rh, Ir, Ru.

(a) increasing ability to hold Cl in $[Me(NH_3)_5Cl]^{++}$ Cr Co Ru Rh Ir →

(b) " basic property of the ion $[Me(NH_3)_5OH]^{++}$ Ru Cr Co Rh Ir →

(c) " acid " " " " $[Me(NH_3)_5H_2O]^{+++}$

Atomic Weight of Ru

Ru has 8 valence steps and none are very stable. The present value of 101.7 is based on the ratio RuO_2: Ru in the compounds $RuCl_3.NO.H_2O$ and $(NH_4)_2[RuCl_5NO]$. Since RuO_2 is not a stoichiometric compound, the value is in dispute. Gleu prepared pure $[Ru(NH_3)_5Cl]Cl_2$ and weighed it in a quartz boat, then reduced it with H_2 to Ru metal at red heat. Gleu set the new value at 101.1 from 11 such measurements.

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Inorganic Seminar March 28, 1939

FLUORINATING AGENTS

Two general methods are available for the fluorination of organic compounds. The first one involves the use of a metallic fluoride such as AgF, TlF, Hg_2F_2, HgF_2, SbF_3 or SbF_3Cl_2 with a halogen substituted alkyl derivative as CCl_4, C_2Cl_6 etc. Antimony pentachloride, iodine, or bromine may be used as catalysts.

The second method is used for introducing fluorine into aromatic compounds. It consists in decomposing diazonium compounds.

1. $C_6H_5N_2HSO_4 + HF \xrightarrow{\Delta} C_6H_5F + N_2 + H_2SO_4$
2. $C_6H_5N_2BF_4 \xrightarrow{\Delta} C_6H_5F + N_2 + BF_3$

The action of elementary fluorine or hydrofluoric acid is in general not very successful. The reaction products are usually tars or inseparable mixtures. However fluorine has been used successfully in some instances, as in the vapor phase fluorination of C_2Cl_6 over copper gauze.

Henne and his coworkers have done a great deal of work in this field, particularly with fluorine derivatives of aliphatic hydrocarbons. He uses SbF_3, SbF_3Cl_2, Hg_2F_2, and HgF_2 as fluorinating agents. The agent used in these reactions must be anhydrous. The preparation of anhydrous mercuric fluoride was formerly carried out by passing fluorine over dry mercuric chloride. Recently Henne has developed a new method which involves passing hydrogen fluoride into a suspension of mercuric oxide in the material to be fluorinated or a solution of this material in an inert solvent. Anhydrous mercurous fluoride is prepared by the action of hydrofluoric acid on mercurous carbonate.

Antimony fluoride in the presence of antimony pentachloride is used to introduce one or two atoms of fluorine into an organic molecule. Mercuric fluoride is a more vigorous agent than antimony fluoride. Three fluorine atoms may be introduced by its use in some cases. In general the yields are [illegible]

Mercurous fluoride is used as a substitute for mercuric fluoride. Its action is less vigorous and not as general as that of the mercuric compounds. In some cases it is converted to the mercuric salt by the addition of iodine.

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Edmond Bottorff

Inorganic Seminar

March 28, 1939

SULFUR MONOXIDE

Sulfur monoxide has only been prepared quite recently, but it's existance has been postulated as an intermediate in many reactions. The reactions in which it has been mostly used are, the formation of polythionic acids from hydrogen sulfide and sulfur dioxide, and in the oxidation of COS.

Schenk's work, especially, has added or detracted from the various mechanisms postulated. The various reactions, where sulfur monoxide was believed to be the intermediate, were studied spectroscopicly. Some of the reactions where sulfur monoxide was found are at present the methods used for the preparation of sulfur monoxide. Of these, the best is the one in which sulfur dioxide is subjected to an electrical discharge. In this way, Schenk has been able to prepare pure sulfur monoxide, and subsequent analysis has established the ratio of sulfur to oxygen as 1:1. Other methods have also been developed.

Schenk and others have also studied the chemical reactions of sulfur monoxide, of which probably the most unexpected is that it will not react with oxygen at normal conditions. As interesting as the above, is the formation of polymers irreversibly. The reactions of sulfur monoxide with unsaturated hydrocarbons, metals, and halogens have also been studied, although in many cases some doubt exists as to what products are formed.

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J. M. Ciskowski

Inorganic Seminar April 4, 1939

Unusual Oxides of Carbon

I. Carbon Suboxide, C_3O_2

A. History

1. Brodie in 1873 submitted CO_2 to action of elec. current. analysis of products showed presence of C_4O_3 and C_5O_4.
2. Berthelot repeated Brodie's work and found that on heating this mixture of oxides CO_2, CO, and $C_{18}O_6$ were formed.
3. Diels and Wolf prep'd. C_3O_2 by treating diethyl malonate with P_2O_5.

B. Preparation:

1. $CH_2(COOC_2H_5)_2 \xrightarrow[300°]{xsP_2O_5} C_3O_2 + 2H_2O + 2H_2C{=}CH_2$
2. $COBr.CBr_2.COBr \xrightarrow{2Zn} C_3O_2 + 2ZnBr_2$
3. $CH_2(COCl)_2 + Ag_2O \rightarrow C_3O_2 + 2AgCl + H_2O$
4. $CH_3CO_2{-}CH{-}CO$ / $CH_3CO_2{-}CH{-}CO$ $>O \rightleftharpoons 2CH_3COOH + C{-}CO$ / $C{-}CO$ $>O \rightarrow C_3O_2 + CO$

   or $CH_3COO{-}C{-}CO$ / $CH{-}CO$ $>O \xrightarrow{\Delta} CH_3COCH$

C. Constitution of C_3O_2:

1. C / C $>C$ / C $>O$ or $O{=}C{=}C{=}C{=}O$

   The diketene type structure is accepted because of characteristic diketene reactions, electron-diffraction, infrared, and Raman spectrum data

D. Physical Properties of C_3O_2:

1. Gas, easily liquefied b.p. + 7°C. at 761 mm. Hg. d= 1.11 (0°C.); solidifies into crystals M.-107° to -111°C. Heat of vap. = 6.08 cal.
2. $C_3O_2 \rightleftharpoons CO_2 + C_2$ K equilibrium = 10^{-7}

E. Chem. Prop. of C_3O_2

1. $C_3O_2 + O_2$ (air) $\rightarrow 3CO_2$
2. Typical diketene reactions:

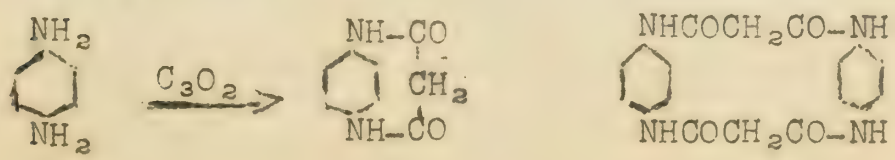
   $O{=}C{=}C{=}C{=}O + 2H_2O \rightarrow CH_2(COOH)_2$
   $+ 2NH_3 \rightarrow CH_3(CONH_2)_2$
   $+ 2PhNH_2 \rightarrow CH_2(CONHPh)_2$
   $+ 2HCl \rightarrow CH_2(COCl)$
   $+ 2Br_2 \rightarrow CBr_2(COBr)_2$

3. $C_3O_2 + H_2S \xrightarrow{vac\ /\ heat} H_2C$ / $CO{-}S{-}OC$ $>CH_2 \xrightarrow{4NH_3} 2H_2C$ / $COSNH_4$ / $COSNH_4$

   $C_3O_2 + xsH_2S \rightarrow H_2C(COSH)_2 \rightarrow COS + CH_3COSH$

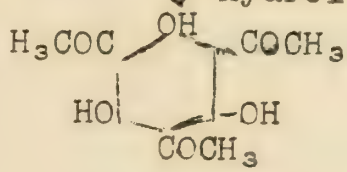
4. $PhNHNH_2 \xrightarrow{C_3O_2} PhNHNHCOCH{=}C{=}O \rightarrow PhN$ / $CO{-}CH_2{-}CO$ $>NH \rightarrow PhN$ / $O{=}C{-}CH_2{-}C{-}OH$ $>N$

5. C / NH_2 / NH_2 $\xrightarrow{C_3O_2}$ $NH{-}CO$ / $C6$ CH_2 / $NH{-}CO$ $\qquad CH_2(COOH)_2 + PhNHNH_2 \xrightarrow[boil]{H_2O}$

6. 

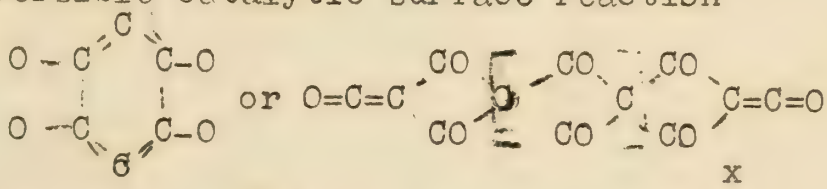
7. Forms add'n cpds with tertiary bases
8. $O=C=C=C=O + SO_2 \text{ -- } CO_2 + O=C=C=S=O$ (polymerizes)
9. $C_3O_2 + NH_2OH \rightarrow CH_2(CONHOH)_2$
   $+ PhNHOH \rightarrow CH_2[CON(Ph)OH]_2$
10. $C_3O_2 + H_2$ catal $H_2C=CH_2$, HAc, CO_2, (C_3O_2)
10. $C_3O_2 + H_2 \xrightarrow{\text{catalyst}} H_2C=CH_2$, HAc, CO_2, $(C_3O_2)_x$
11. With amines, C_3O_2 gives substituted malonamides $(CH_3(CONRR')_2)$
    R and R' = H, R, Ph, subs. Ph, amino ester.
12. Reactions with D_2O to give $CD_2(CO_2D)_2$ and CD_3CO_2D
13. $3O=C=C=C=O + 3CH_3MgI \rightarrow 3CH_3C(OMgI)=C=C=O$

↓ hydrolysis and condensation



F. Polymerization of C_3O_2:
1. This is an irreversible catalytic surface reaction

polymer may be:



G. Analysis of C_3O_2 in mixture of CO_2, CO, O_2.
The C_3O_2 reacts with $H_2O \rightarrow$ malonic acid
Tirtrate with $Ba(OH)_2$ after freezing out $CO_2 + H_2O$

II. Other Oxides of Carbon
Klemenc and Wagner state that 3% yield of C_5O_2 is formed on decomposition of C_3O_2. The C_5O_2 can be isolated and purified by isothermal dist'n. Properties: M.P. below -100°.
B.P. (calc'd) $105^+ - 3°$. V.P. (calc's) 419 mm 0°C
235 67.7
159 86.6

Analysis: (1) $C_5O_2 + H_2O \rightarrow CO_2 + C_{18}H_{16}O_{12}$
$\rightarrow$ titrate with $Ba(OH)_2$
(2) C_5O_2 heated with CuO, gaseous products frozen, and det'd. as above.
Otto Diels questions the existence of C_5O_2 on possibilities of incorrect analysis poor explanation of react. with H_2O, and unreasonable v.p. and b.p.
Klemenc and Wagner, mention possibility of formation of C_3O_4 and C_3O_6 when C_2 reacts with O_2.

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Bernard Dudenbostel

Anorganic Seminar April 4, 1939

Isotopes of Potassium

J. J. Thomson, in 1905, discovered that potassium is a radioactive element.

F. W. Ashton, in 1921, discovered that potassium has two isotopes. This led to many experiments to determine which isotope is radioactive. Between 1921 and 1935 many experimenters reported on this topic but none obtained any definite proof and the conclusions are postulations that the radioactivity may be due to K^{41} or other isotopes of potassium such as K^{40}, K^{42}, or K^{43}

Finally in 1935 A. O. Nier discovered the K^{40} isotope. This was confirmed by Brewer later in the same year. They found that K^{40} constituted about one part in 8300 of ordinary potassium. Smythe and Hemmendinger, in 1937, studied the isotopes of potassium and found that K^{40} is responsible for the entire known radioactivity of potassium Bramley and Brewer investigated the K^{40} isotope and have given values for the disintegration constant ($\theta = (1.56 \pm 0.6) \times 10^{-17} sec.^{-1}$), the average life ($\lambda = 20.3 \times 10^{8}$ hr.), and the half-life ($T = (14.2 \pm 3.0) \times 10^{8}$ yr.).

Brewer has carried out a pretty thorough investigation of the relative abundance of the isotopes in mineral, plant, and animal materials and in his last report the following values are given.

Isotope	Present Relative abundance	Initial Relative abundance
K^{39}	8,300	8,300
K^{40}	1	12,534
K^{41}	585	585

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Ed Dunlop

Inorganic Seminar September 28, 1939

Intermetallic Compounds

General:

The first indication that two metals might actually unite to form a compound was given in 1839 when it was noticed that the action of acids on alloys of Cu and Zn showed a discontinuity at the point at which the two metals were in equal proportions. Previous to this time "intermetallic compounds" were considered to be anomalies. In 1897 the "freezing-point curve" method of studying alloys was introduced, and in 1923 the first crystal structure determination of an intermetallic compound was made. Since then a great deal of work has been done in this field.

The problem is an extremely difficult one and "principles" which were considered fundamental in nature at one time are now under question. About twenty years ago intermetallic compounds were defined with confidence. Now there is no general agreement as to what actually constitutes such a compound. Some research workers, in fact, prefer not to use the term intermetallic compound at all, but rather to employ the term "intermediate phase." It seems quite certain that these intermetallic compounds, or intermediate phases, in the solid state contain no "molecules" as such. The conception of a molecule fails here just as in the case of solid sodium chloride.

Three methods of investigation--the X-ray, the thermal, and the microscopical--are of primary importance in the study of these compounds. Other methods such as measurements of electrical and magnetic properties and chemical reactivity, although valuable in themselves and sometimes indispensable, are subsidiary to these three in the range of their applicability.

Classification of Intermetallic Compounds:

The problem of classifying intermetallic compounds is very difficult. The experimental difficulties are not only great, but as yet no single theoretical or empirical method of treatment has been sufficiently powerful to elucidate more than a portion of the entire field. Finally, intermetallic compounds form solid solutions with each other and with their constituent elements giving rise to new and complicating alloy phases.

Intermetallic compounds include not only substances which are typically metallic in their nature but also others which constitute definite transitions between the metallic linkage on the one hand and both the covalent and electrovalent linkages on the other. The frequent multiplicity of compounds derivable from a single pair of element and the apparent failure of these compounds to follow any of the familiar rules of valence has resulted in considerable speculation as to the nature of the binding forces involved and the fundamental constitution of these compounds.

A semblance of order was introduced into this field by Hume-Rothery in 1926 as a result of work carried out with certain alloys of Cu, Ag, and Au. The generalizations enunciated at that time have since found wider applications and while these principles are not

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General:

The first indication that two metals might actually unite to form a compound was given in [illegible] when it was noticed that the series of [illegible] alloys of Cu and Zn showed a discontinuity at the point at which the two metals were in equal proportions. [illegible] "intermetallic compounds" were considered to be [illegible]. In [illegible] the "thermal-point curve" method of studying alloys was introduced, and in [illegible] the first crystal structure determination of an intermetallic compound was made. Since then a great deal of work has been done in this field.

The problem is an extremely difficult one and "principles" which were considered fundamental in nature at one time are now under question. About twenty years ago intermetallic compounds were defined with confidence. Now there is no general agreement as to what actually constitutes such a compound. Some research workers, in fact, prefer not to use the term "intermetallic compound" at all, but rather to employ the term "intermediate phase". It seems quite likely that these [illegible]

Three methods of investigation, the X-ray, the thermal, and the microscopical, are of primary importance in the study of these compounds. Other methods such as measurements of electrical and magnetic properties and chemical reactivity, although valuable in themselves and sometimes indispensable, are subsidiary to these three in the range of their applicability.

Classification of Intermetallic Compounds:

The problem of classifying intermetallic compounds is very difficult. The theoretical difficulties are not only great, but as yet no single theoretical or empirical method of treatment has been sufficiently powerful to give more than a partial [illegible] of the entire field. Finally, intermetallic compounds form solid solutions with each other and with their constituent elements giving rise to new and complicating alloy phases.

Intermetallic compounds include not only substances which are essentially metallic in their nature but also others which constitute definite transitions between the metallic linkage on the one hand and the covalent and electrovalent linkage on the other. The frequent multiplicity of compounds derivable from a single pair of metals and the apparent failure of these compounds to follow any of the ordinary rules of valence has resulted in considerable speculation as to the nature of the binding forces involved and the fundamental conditions of their existence.

A [illegible] was introduced into this field by Hume-Rothery in 1926 as a result of work carried out with certain alloys of Cu, Ag, and Au. The generalizations [illegible]

universally valid they hold good for a large number of systems and undoubtedly represent a general principle.

An indication as to the regularities underlying the formation of intermetallic compounds in many systems was given by the observation that in a considerable number of cases, although the formulas of the intermetallic compounds differ entirely from one another, the systems pass through the same sequence of crystal structures as the proportions are varied. This succession of phases may be illustrated by the Cu-Zn alloys. Copper itself has a face-centered cubic structure. On adding Zn to it, there are at first formed solid solutions of the same structure, in which Cu is replaced atom for atom by Zn. When the limit of this simple solid solution is reached, a phase with the body-centered cubic structure appears, known as β - brass, and approximates the formula CuZn. This in turn gives place to a so-called γ -phase, possessing a complicated crystal structure, which may be formulated Cu_5Zn_8. The next phase to appear as more Zn is added, the ϵ - phase, with a hexagonal close-packed lattice, has the composition $CuZn_3$.

The same succession of phases on passing from 100% of the element of lower valence to 100% of the element of higher valence, i.e. face-centered cubic (α -phase) ------→ body-centered cubic (β -phase) -------→ γ -phase ------→ hexagonal close-packed (ϵ -phase), reappears in numerous other cases, and the intermetallic compounds described in the literature represent the rationalized formulation of these characteristic structures. The formulas of β, γ and ϵ -phase in a few systems are given below.

System	β -phase	γ -phase	ϵ -phase
Cu--Zn	CuZn	Cu_5Zn_8	$CuZn_3$
Cu--Sn	Cu_5Sn	$Cu_{31}Sn_8$	Cu_3Sn
Ag--Cd	AgCd	Ag_5Cd_8	$AgCd_3$
Co--Zn	$CoZn_3$	Co_5Zn_{21}	
Cu--Cd		Cu_5Cd_8	$CuCd_3$
Cu--Al	Cu_3Al	Cu_9Al_4	
Pt--Zn		Pt_5Zn_{21}	
Na--Pb		$Na_{31}Pb_8$	
Ratio of valence electrons to atoms:	3:2	21:13	7:4

The Hume-Rothery Rules: The common structural principle underlying the apparently erratic composition of these characteristic intermediate phases was perceived by Hume-Rothery to be the ratio between the number of valence electrons and the total number of atoms in the compounds. These ratios have the values 3:2, 21:13, and 7:4 for the β, γ and ϵ -phases, respectively. Thus, in Cu_5Sn (6 atoms), if each Cu contributes one electron and Sn four electrons, there are nine electrons in all. Similarly in the γ -phase $Cu_{31}Sn_8$ (39 atoms) there are 31 + 8 x 4 = 63 electrons, and in the ϵ -phase Cu_3Sn (4 atoms) there are 3 + 4 = 7 electrons. All the compounds listed above conform to this rule, Cu, Ag, and Au always being univalent, Sn and Pb quadrivalent, etc. The transition elements fit this scheme only if they contribute no valence electrons.

In attempting to understand the significance of these most interesting relations, it must be emphasized that they are at present restricted to one particular series of alloys, those of Cu, Ag, and Au, and that there are most certainly exceptions to the general rules. It cannot be doubted that other factors, and particularly the atomic radii, influence the type of crystal structure, but on the whole it does not seem unreasonable to conclude that, when other conditions are favorable, the type of crystal structure in this series of alloys is determined principally by the ratio of atoms to valence electrons.

Theoretical Basis for the Hume-Rothery Rules:

The above empirical relationships between crystal structure and electron density have recently been given a quantum mechanical explanation which points to a more fundamental understanding of the metallic state. According to this explanation the valence electrons occur in bands of permitted energy in crystals and the breadth of each band will be dependent in some way upon the crystal structure since this determines the number and distribution of nearest neighbors to any one atom. Considered from this standpoint, the energy bands within which an electron may be transferred from one state to another without involving any large jump in energy are usually termed Brillouin zones. For each type of crystal structure the number of electrons per atom which may be accommodated within the lowest Brillouin zone is a calculable quantity. If electrons are fed successively into a metallic crystal lattice, they will therefore take up states of gradually increasing energy until the lowest Brillouin zone is filled. The next electrons must be placed in the next available Brillouin zone, and will lie, in general, at considerably higher energies.

Before the Brillouin zone is quite filled, however, there comes a stage where the energy begins to increase rapidly as more electrons are added, marking the point where the tendency appears to over flow into the next Brillouin zone. Alternatively, it may be possible for the crystal structure itself to change so as to accommodate more electrons per atom in the lowest zone without crowding. This, indeed, is the explanation of the remarkable Hume-Rothery ratios in the succession of phases in binary alloys. If Zn is added to Cu, this in effect is equivalent to adding electrons to the lattice without changing the number of atoms, since Zn is divalent and Cu is univalent.

The theory qualitatively outlined above leads to the conclusion that the transitions

α -phase $\longrightarrow$ β -phase $\longrightarrow$ γ -phase $\longrightarrow$ ϵ -phase

should occur at 1.362, 1.480, 1.538, and 1.75 electrons per atom respectively. A comparison of this conclusion with the observed compositions, and with Hume-Rothery's rationalized ratios, apparently gives a convincing picture of the mechanism operating in the formation of these intermetallic compounds.

Properties of Intermetallic Compounds:

In general the electrical conductivity of a definite intermetallic compound is always less than that of the better conducting of its two component elements and is usually less than that of either element.

The thermal conductivity follows the electrical conductivity in being generally lower than that of its constituent metals and is comparable to that of the non-metals in certain cases.

The hardness is usually greater than that of either of its generators. The compound Cu_3Sn is about 12 times as hard as Cu.

In their stability toward heat the commonly accepted intermetallic compounds vary between wide limits.

They manifest considerable variation in chemical reactivity. A great number are considerably less reactive than the most reactive of their components but some are so reactive as to oxidize in moist air, falling to white powders. Some are spontaneously inflammable when rubbed.

The melting points of the intermetallic compounds as compared with the melting points of the component metals seem to depend considerably on the heats of formation of the compounds.

These compounds are as a rule less ductile and malleable than the component metals.

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R. N. Keller

Inorganic Seminar October 3, 1946

"SELENIUM OXYCHLORIDE"

Preparation (1)

$SeOCl_2$ was first prepared by Weber in 1859, by heating together $SeCl_4$ and SeO_2. The general methods for its preparation today are represented by the following equations: (1) $SeCl_4 + SeO_2 \rightarrow 2SeOCl_2$; (2) $SeCl_4 + H_2O \rightarrow SeOCl_2 + 2HCl$; (3) $SeO_2 \cdot 3HCl \rightarrow SeOCl_2 + H_2O$.

Properties (2)

Its physical properties somewhat resemble those of water. It boils at 179° C. and melts at 8.5°, so it is a liquid at ordinary temperatures. It is yellow as ordinarily prepared but colorless when pure. The electrical conductance is low. The specific conductance at 28° with carbon electrodes is 9.6×10^{-4} ohms. It is transparent to visible light but opaque to ultraviolet. It makes a perfect screen for light of wave lengths less than 4050 A°. It has a dielectric constant of 46 at 20°. It is miscible in all proportions with CCl_4, $CHCl_3$, CS_2, and C_6H_6. These are true mixtures as they can be separated by distillation. Selenium oxychloride reacts with or dissolves an exceptionally large number of elements and compounds. Of the non-metals it dissolves S, Te, Se, red P, Br, and I, while B, Si, and C are not attacked. Most all of the metals are attacked forming the metal chloride and Se_2Cl_2. They are, K, Al, Zn, Bi, Sn, Cu, Ca, Mg, Cr, Pb, Ni, As, Cd, Co, Au, Pt, Fe, Ag, and Sb. The few not attacked are Na, W, Ta, and Ti. Separations of Na and K, Many oxides are also attacked, among them the oxides of As, V, Ni, Co, TeO_2, Fe, Mo, Cu, Ag, and PbO. These are attacked in the cold. The not attacked are Al, Th, R.E., Ti, Cb, Ta, Zr, TeO_3, and W. Thus V may be separated from Cb and Ta; Mo from W; and TeO_2 from TeO_3. If SO_3 is added to the $SeOCl_2$ its solvent action is more powerful, dissolving the oxides of Al, Cr, R.E., Ti, Cb, and U. It does not dissolve Zr, W, and Ta. Thus Ti may be separated from Zr; Cb from Ta; and U from V. All of these separations are rather difficult to completely effect chemically. Many carbonates and sulphides are also soluble.

In the organic field $SeOCl_2$ is also an exceptional solvent. It dissolves aliphatic unsaturated hydrocarbons with the formation of compounds of the general formula $(ClC_nH_{2n})_2SeCl_2$ and the evoluation of SeO_2. Saturated aliphatic hydrocarbons are not acted on. Aromatic hydrocarbons are extremely soluble and may be recovered unchanged by distillation. Protein containing materials such as hair, silk, bristles, and leather are soluble as are carbohydrates. Phenolic condensation products such as Redamol, bakelite, and condensite are also soluble; also gums, resins, paints, lacquers, shellac, varnish, agar, glue, celluloid, and gelatin. Natural asphalts, resins, and bitumens, are easily soluble. Natural rubber vulcanized rubber, and synthetic rubber such as isoprene are soluble. $SeOCl_2$ was the reagent used in helping to establish the structure of rubber by showing that the structure of polymerized isoprene was essentially the same as natural rubber. $SeOCl_2$ reacts with the bituminous and resinic material in natural coals leaving a carbonaceous residue.

Selenium oxychloride as a non-aqueous solvent.

The Bronsted concept of acids and bases extended by G.B.L. Smith (3) to include all solvents. He proposes the following definition: "A solute is an acid when its molecule (neutral or charged) is an electron pair acceptor toward the molecule or an ion of the solvent; on the other hand, a solute is a base when its molecule (neutral or charged) is an electron pair donor towards the molecule or ion of the solvent." It is postulated that $SeOCl_2$ ionizes as follows $SeOCl_2 \rightarrow (SeOCl)^+ + Cl^-$. This is based on such evidence as the conductance of the pure liquid, the products formed in electrolysis, the products formed when $SeOCl_2$ reacts with metals, the composition of some solvates, and some metathetical reactions which have been carried out in $SeOCl_2$.

Although $SeOCl_2$ is not a good conductor, if it is electrolyzed chlorine is obtained at the anode and selenium monochloride at the cathode. If KCl in $SeOCl_2$ is electrolyzed, chlorine is obtained at the anode and SeO_2 at the cathode. If $SnCl_4$ is used as the electrolyte, chlorine is still obtained at the anode but both SeO_2 and Se_2Cl_2 are obtained at the cathode. On the basis of these observations the electrode reactions are postulated as: anode reaction $2Cl^- + 2e \rightarrow Cl_2$; cathode reaction $6(SeOCl)^+ + 6e \rightarrow 6SeOCl$, this compound being very unstable undergoes an immediate change as $6SeOCl \rightarrow 2SeO_2 + Se_2Cl_2 + 2SeOCl_2$.

The action on a metal is given by $4SeOCl_2 + 2Cu \rightarrow 3CuCl_2 + Se_2Cl_2 + 2SeO_2$. The following reactions are in accord with both the above reaction and the known facts of electrolytic decomposition: $3\ Cu + 6(SeOCl)^+ \rightarrow 3Cu^{++} + Se_2Cl_2 + SeO_2 + 2SeOCl_2$ then $3Cu^{++} + 6Cl^- \rightarrow 3CuCl_2$. This further shows that $SeOCl_2$ is a strong oxidizing agent.

The chlorides of non-metals and of the amphoteric metals are considered as acids in $SeOCl_2$. They all form solvates e.g. $SnCl_4.2SeOCl_2$. If these substances are formulated in accordance with the usual ionic forms, we find that this formulation is consistent with the postulation regarding the autoionization of the parent solvent, i.e. $(SeOCl)_2^{++} + SnCl_6^{--}$. As previously stated the addition of SO_3 to the $SeOCl_2$ greatly increases its solvent power. It is evident that this is a chlorosulfonic acid of the selenium oxychloride system $(SeOCl)(SO_3Cl)$. Molybdic oxide also appears as a acid in selenium oxychloride $(SeOCl)(MoO_3Cl)$. Stannic chloride acts as an electron pair acceptor toward chloride ions as follows: $SnCl_4 + 2Cl^- \rightarrow SnCl_6^{--}$.

Ammonia is regarded as a typical base and its reaction with water is $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$. The reaction between ammonia and selenium oxychloride seems entirely analagous as $NH_3 + SeOCl_2 \rightarrow NH_3SeOCl^+ + Cl^-$. Pyridine and quinoline also act as bases in selenium oxychloride.

Reactions in seleneium oxychloride.

Pyridine being a base and stannic chloride being an acid in selenium oxychloride, it should be possible to titrate them. Pyridine was titrated electrometrically with the stannic chloride and a break in the curve was obtained which corresponds to 2 mols of pyridine to one of stannic chloride. $CaCl_2$ was titrated with $SnCl_4$ and three inflection points in the curve were obtained corresponding to the salts $Ca[(SeOCl)SnCl_6]_2$, $CaSnCl_6$, and $Ca_3(SnCl_7)_2$. Pyridine and ferric

chloride gave three inflection points corresponding to the primary secondary, and tertiary salts: $(C_5H_5NSeOCl)(SeOClFeCl_5)$, $(C_5H_5NSeOCl)_2(FeCl_5)$, and $(C_5H_5SeOCl)_3(FeCl_6)$. Pyridine and sulphur trioxide gave two inflection points corresponding to the salts: $(C_5H_5SeOCl)SO_3Cl$ and $(C_5H_5SeOCl)_2SO_3Cl_2$.

The Separation of Tb and Pr from a mixture of the Rare Earths.

Of the 17 rare earths, only five at present, may be separated from their neighbors by special means. These are: Sc by means of the complex fluoscandiates, Eu, Yb, and Sm by reduction to the divalent state, and Ce by oxidation to the tetravalent state. In spite of many attempts, no way has been found, until the present, to separate Pr and Tb through oxidation to the tetravalent state.

It is known that the rare earth oxides and hydroxides are soluble in fused alkali, especially KOH, but that the tetravalent oxides of Pr, Ce, and Tb are not. If these members could then be oxidized in fused alakli they could be separated from the others. Beck (4) accomplished this electrolytically by dissolving a mixture of rare earth oxides in fused KOH. Ce, Pr, and Tb separated at the anode in the the tetravalent state and could be separated from the melt. To test the effectiveness of this method Beck used 10 gms. of commercial didymium oxide. This was fused with KOH in a nickel crucible which was connected to the positive pole of a battery of 4 volts potential. A Pt wire dipped in the melt served as a cathode. 0.5-0.7 amps were passed through the solution for 30-40 minutes. The heavy PrO_2 formed sinks to the bottom of the crucible and can be easily separated from the soluble Nd_2O_3 by simple decantation of the melt. To complete the removal, the melt is allowed to cool and extracted with water. The Nd is hydrolyzed to the insoluble hydroxide and the Pr is unaffected. The solid suspension is centrifuged and the Pr sinks to the bottom. The $Nd(OH)_3$ is extracted with HAc leaving the insoluble PrO_2. The stronger the HAc used the more complete is the separation of Pr from Nd. It is possible to prepare praseodymium free neodymium in one operation but not the Nd free Pr. This explained by assuming that instead of simple PrO_2 being formed the salt $Pr(PrO_4)$ is formed. It is assumed also that some $Nd(PrO_4)$ is formed which is also insoluble, thus contaminating the Pr fraction.

In an attempt to separate the Tb from a Tb-Sm-Gd-Eu mixture by electrolysis, it failed completely because the Eu was reduced at the cathode to the divalent state and hindered the oxidation of the Tb. If, instead of electrolytically oxidizing the Tb one uses fused $KClO_3$ the oxidation and separation is more complete. In order to arrive at such an enriched Tb preparation by previously used methods, over 1,000 fractionations were necessary and the Tb was distributed over many fractions; while the present method, after three operations one has about the same amount of Tb in one fraction.

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Thos. O'Brien

Low Temperatures

Temperatures to 1° K.

The attainment of low temperatures grew out of liquefying gases since the critical temperatures were fairly low. Then the work turned to keeping low temperatures for periods long enough to study properties. This was done at first by reducing the pressure on a boiling liquid to a constant value. By using different liquefied gases, temperatures down to the freezing point of N_2 could be maintained. Temperatures below 50°K had to be obtained in some other manner.

Simon solved the problem for temperatures from 50°K to below 4°K with an apparatus for the desorption of helium from charcoal. He gas is absorbed on charcoal and after the space surrounding the charcoal is cooled and evacuated, then the He on the charcoal is pumped off cooling the system. The vacuum insulation is capable of maintaining low temperatures for several hours. Very little He is required in the whole process.

Ruhemann has introducee a miniature Linde liquefier to reach and maintain constant temperatures between 9°K and 1°K. Disadvantage compared to Simon's apparatus -- very pure gas must be used to prevent blocking valves.

Ruhemann and Lichter at Kharkov studied the use of eutectic mixtures for low temperatures. They found that an N_2, O_2 mixture gave a temperature of 50.1°K at a concentration of 22% O_2. Methane and ethylene had an eutectic temperature of 84.5°K at 12.2$_5$ C_2H_4. Further study may lead to others with lower temperatures.

Temperatures below 1°K

Temperatures below 1°K have been obtained by what is called the magneto-caloric effect, discovered by Weiss in iron in 1921. If a paramagnetic substance is placed in a magnetic field, the temperature of that substance rises and when the field is shut off, the substance cools again.

In the Simon and Kürti apparatus, the paramagnetic material is packed loosely in a thin-walled glass tube containing 1 cc. He at room temperature and sealed off. The capsule is placed in liquid He and the magnetic field of 8000 gauss turned on. After equilibrium, the He surrounding the capsule is drawn off and then the field is turned off. A perfect vacuum is formed since all the He left solidifies at once. The rate of warming is .0003°/min.

By the magneto-caloric method the following low measurements have been obtained:

Giaque and MacDougall	$Gd_2(SO_4)_3 \cdot 8H_2O$	.25°K	Berkeley
Simon and Kürti		.1	Oxford
Allen and Shire	$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	.027	Cambridge
de Haas and Wiersma	CeF_3	.15	Leyden
	$Dy(EtSO_4)_3$	.09	
	$Ce(EtSO_4)_3$	.08	
	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	.0044	

$K_2SO_4.Cr_2(SO_4)_3.24H_2O$ .0044

Thermometers to 1°K

The most common method of measuring low temperatures is a gas thermometer, either a constant pressure or constant volume type. In practice the constant volume type has proved better. The pressure on such a thermometer decreases 1/273 for each degree drop in temperature. This is a primary the primary standard thermometers down to about 5° K using He gas.

Practically secondary standards of three kinds are used: vapor pressure, thermocouple, and resistance thermometers.

Vapor pressure curves are very steep for the permanent gases near their boiling points so they are quite accurate. But this steepness means that they can be used only over a small range. Advantage- vapor pressure is independent of the amount of substance in each phase so the volume of the manometer and connecting tubes need not be known. They work best at low temperatures - down to 1°K.

Thermocouples are not used for accurate work. The sensitivity below the boiling point of H is small becuase thermoelectric forces between the joints of the two metals fall off rapidly at low temperatures. Thermocouples in order of usefulness are Cu-consstantan, Fe-constantan, Au-Ag.

A resistance thermometer of phosphor bronze is the best secondary thermometer because of its high coefficient of resistance at low temperature. Pt works very well because its resistance is a simple quadratic function. These thermometers consist of thin wires rolled without strain around unglazed porcelain frames. A potentiometer is used to measure R_t.

Thermometers below 1° K.

The only sould basis for measuring the temperature below 1°K is by a thermodynamic scale. But until the magneto-caloric effect is better understood, an arbitrary scale is used assuming that Curie's law holds (Curie's law XT = C, where X = susceptibility). The susceptibility may be measured with a magnetic balance by finding the force exerted on the sample in an unhomogeneous field. Because of the moving parts on the balance, it is less accurate than an inducation method. The essential features of this method are two coils surrounding the specimen in separate circuits. The induction in the secondary is measured when the current is turned on or off in the primary.

Extremely low temperatures result in superconductivity in some metals. The temperatures at which some become superconductors is given in the table below:

Nb	8.4K°	Hg	4.12 K°	Ti	1.77 K°	Zn	.79°K
Pb	7.26	Sn	3.69	Th	1.43	Zr	.70
La	4.71	In	3.37	Al	1.14	Cd	.60
Ta	4.38	Tl	3.38	Ga	1.10	Hf	.3-.4

Au, Cu, Bi, Mg, Ge did not become superconductors down to .05° K.

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INORGANIC SEMINAR October 17, 1939

TEH SEPARATION OF ISOTOPES

Since F. W. Aston's announcement in 1913 that a partial separation of the isotopes of neon had been effected, many attempts to separate the isotopes of the stable elements have been made. Although the methods which have been developed leading to the partial or complete separation of isotopes are of interest in themselves, there are many important applications of the results of such separation in chemistry, physics and biology. Quoting Aston""in physics all constants involving e.g. the density of mercury or the atomic weight of silver may have to be redefined while in chemistry reconstruction may be necessary for that part of the science the numerical foundations of which have hitherto rested securely upon the constancy of atomic weights." There are also many problems in the fields of unclear transformations, radioactivity, and spectroscopy which can be completely or partly solved by using separated isotopes. The use of fractioned isotopes as indicators in the study of chemical exchange reactions and biological processes is becoming of increasing importance and in this type of work even partly separated isotopes will in many cases provide a useful tool.

I. Separation by Means of Mass-ray Analysis

This method of separation depends upon the fact that the deflection of a beam of ions in a magnetic field is dependent upon its mass. The first successful results were reported in 1934 by Crowther working in the Cavendish laboratory. Steady improvements have been made in the design and operation of the spectrograph and it may now be said that the method gives separated isotopes of a high degree of purity. The yields are low and of no use in chemical experiments but of value for certain physical purposes.

II. Separation by Means of Diffusion Methods.

a. G. Hertz was the first to successfully use the physical principles involved in the diffusion of gases through porous pipeclay. By using a battery of fifty fractionating units pure H^1, D^2 and Ne^{22} were obtained. Many other excellent separations have been made and this may be considered as one of the more important methods.

b. Gravitational diffusion based upon separation by centrifuging is in an embryonic stage but appears promising. Use is made of a vacuum type tubular centrifuge using e.g. Cl_2, or CCl_4 in the vapor state.

c. Thermal diffusion methods are being developed and to date have given e. g. a gas consisting of 40% HCl^{37}. Ordinary HCl has 27% HCl^{37}.

III. Electrochemical Methods

Electrochemical methods have been highly successful in the separation of hydrogen and deuterium but have not been too encouraging in the separation of O^{18}. Li^6 + Li^7 -- mercury cathode

IV. Separation by Means of Fractional Distillation

Only slight separation has been effected in the preliminary experiments with water, liquid ammonia and air, and neon. The concentration of heavy oxygen from water however is sufficient for the study of oxygen exchange reactions in solution.

V. Separation by Chemical Exchange Methods.

Li amalg. + Li^+ $\longrightarrow$ Li^6 goes to the amalgam

This method of separation depends upon the fact that slight differences in the chemical properties of isotopic compounds of the lighter elements should exist. For example in the equilibrium

$$^{15}NH_3(gas) + {}^{14}NH_3(sol'n) \rightleftharpoons {}^{14}NH_3(gas) + {}^{15}NH_3(sol'n)$$

the concentration of ^{15}N in the $^{15}NH_3$ solution is favored. By making use of a continuous counterflow of liquid and gas, high efficiency is achieved. A column has been designed to give a production of 1.5 g. of N^{15} per 24 hours in concentrations of 60%. This method is one of the most important.

VI. Separation by Photochemical Means.

A photochemical method has been used to effect a partial separation of Hg^{200} and Hg^{202} by selective irradication of ordinary mercury vapor with two components of the mercury resonance line at 2537A. This particular method has received practically no study.

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(There are 66 other references listed under this article.)

Lester A. Brooks

INORGANIC SEMINAR November 21, 1939

The Phase Rule

Gibbs published a classical paper "On the Equilibrium of heterogeneous Substances" in the obscure "Transactions of the Connecticut Academy". This paper was based on the principles of thermodynamics and was published in abstract mathematical language with very few practical applications. Gibbs' work was first recognized in Europe, where it was translated into German by Ostwald. It remained for Roozeboom to derive the phase rule from the work of Gibbs.

The phase rule is a mathematical expression of the number of degrees of freedom, the number of components, and the number of phases of a system. It applies only to systems in a condition of chemical equilibrium. It is necessary to define these quantities accuretely.

Phases:- A phase is a homogeneous portion of matter which is physically distinct and mechanically separable from other phases. There can be only one gas phase, and a solution is only one phase, but a mixture of crystals of different kinds contains as many phases as there are kinds of crystals in it. Equilibrium is considered to be independent of the amounts of the phases and therefore the phase rule is not applicable when the volume of a phase is so greatly reduced that surface tension forces come into play.

Components:- It is moredifficult to decide the number of components in a system then it is to decide the number of phases. By the components of a system we mean only those constituents which can undergo independent variation in the different phases. Also as the number of components there is to be chosen the smallest number of inedpendently variable constituents by means of which the composition of each phase taking part in the equilibrium can be expressed by means of a chemical equation. The number of components may change with alteration of the conditions of the experiment.

Degree of Freedom: - The number of degrees of freedom of a system is the number of variable factors which can include temperature, pressure and the concentration of the components, which must be arbitrarily fixed in order that the condition of a system may be perfectly defined.

A knowledge of the number of degrees of freedom (sometimes called the variability) is essential in studying a system, and the real merit of the phase rule is that the state of the system is defined entirely by the relation between the number of components and the number of phases without the use of any assumptions concerning the constitution of matter, and no assumptions of the molecular complexity of the substances in equilibrium.

Derivation of the Phase Rule: - Substances in equilibrium have the same chemical potential (for the same component in both phases). and the potential of a substance in any phase depends on the composition of the phase and on the temperature and pressure. If we have n components in r phases, then to fix the composition of unit mass of each phase we must know the composition of (n - 1) components in each phase. As regards composition therefore each phase possesses (n - 1) variables. There are also two other variables, temperature and pressure which are, of course, the same for each phase in equilibrium. Therefore the system of r phases possesses,

$$r(n-1) + 2 \text{ variables}$$

To define the state of the system completely we require as many equations as there are variables. If we have fewer equations than we have variables, then according to the deficiency in the number of equations, one or more variables will have an undefined value, and therefore values must be assigned to these variables before the system is entirely defined. The variability or the number of degrees of freedom of the system is the number of these undefined variables.

These equations are obtained from the chemical potential of a component in a phase, its temperature and pressure. When we have equilibrium between phases, the chemical potential of a component of a substance is the same in all of the phases in which it occurs.

We choose a standard phase in which are included all of the components. For each phase in equilibrium with it there will be a definite equation of state for each component in it. Therefore if there are r phases, we obtain for each component (r - 1) equations, and for n components n(r - 1) equations.

We have therefore r(n - 1) + 2 variables and only n(r - 1) equations. Therefore we have: -

$$r(n-1) + 2 - n(r - 1) = n + 2 - r$$

variables undefined. That is the degree of freedom of a system is defined as: -

$$F = n + 2 - r$$

Although it is possible to use mathematical equations to express the conditions of equilibrium, the practical application of the phase rule is greatly simplified by the use of phase diagrams. In the case of one component systems we can use rectangular coordinates whose axes are temperature and pressure. With two components one axis can be used to represent the % of one component while the other axis can be temperature, when we use a constant pressure diagram or the reverse, or we can have a solid model in which the third axis represents pressure.

In the case of three component systems it is usual to have the three components at the three corners of an equilateral triangle, the temperature axis being vertical to the plane of the triangle and the pressure assumed to be constant. In certain cases where two components are salts which form hydrates and the third component is water, we use rectangular coordinates, the lengths along the axes being measured as grams of anhydrous salt per 100 grams total, the water being given by difference.

<u>One Component Systems:</u> - From the phase rule it is seen that we have a maximum of two degrees of freedom. This will be the case when we have only one phase. With two phases we have one degree and with three phases no degrees of freedom. The theorem of Le Chatelier extends the scope and practical utility of the phase rule. It is of value in predicting what will happen to a particular system on increasing the temperature or the pressure.

<u>Two Component Systems:</u> - These are more important then the one component systems in practice and the relations are, of course, more complicated. They are of especial importance in the study of alloys. Here we often have solid solutions. These are of different types. We can have the type where all solid solutions are miscible in all proportions, and also the types where the solid solutions are not completely miscible. The latter is of two types (a) where the freezing point curve shows a trsnsition point and (b) where it shows a eutectic. The former is of three types (a) minimum melting point (b) maximum melting point and (c) all solid solutions melt between the melting points of the components.

Practical Applications of the Phase Rule: -- The phase diagrams form a convenient form in which to record experimental data on solubility, and melting points or vapor pressures of systems of more than one component which would otherwise make very cumbrous tables.

One of the most important practical applications of the phase rule was in the study of Searles Lake brine. It was found impossible to obtain potassium chloride by the evaporation of the brine by means of the heat of the sun, and it was also impossible at 100° C. This is due to the fact that double salts are formed, and this accounts for many failures. When the phase diagrams were constructed, and the differences for the diagrams at 100° and at 20° were noted, a method of obtaining potassium chloride was developed. It consists in evaporation until a certain point at 100°, then cooling to 20° C., and further evaporating at 20° C. to remove the potassium chloride.

Another interesting phase rule study is the study of systems made by fusing and then slowly cooling mixtures of lime, alumina and silica, One such system is known as Portland Cement. This system was very difficult to study since it necessitated very high temperature measurements and anslyses of the crystals separating from each melt at different times.

One of the most important alloys is that of carbon and iron. Here a complication is introduced since iron can exist in three different phase modifications. These are known as alpha, gamma and delta ferrite. Alpha ferrite is in the form of a body centered cubic latice and is the stable form below 900°. Gamma ferrite is the stable form between 900 and 1400°. It is in the form of a face centered latice. Delta iron has a body centered latice, differing in size from that of alpha ferrite, and it is the stable form above 1400°. Beta ferrite is not a phase modification but a magnetic modification and its formation is a progressive transformation and not a change at any definite temperature.

Phase diagrams are also of value in deciding whether compounds are formed in certain systems. Examples are hydrates, intermetallic compounds, racemic compounds, etc.

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INORGANIC SEMINAR November 28, 1939

PROTECTIVE COATINGS FOR METAL SURFACES

Introduction:

Corrosion may be defined broadly as the chemical action of certain external agencies on metals which cause their deterioration or destruction. Numerous theories as to the cause of corrosion have been proposed, of which the following are the more important:

(a) Acid Theory - Calbert, 1871

$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2$

$4FeCO_3 + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2CO_3$

$H_2 + 1/2O_2 \rightarrow H_2O$

(b) "Auto-colloid Catalytic Theory" - Friend

This theory postulates the formation of an intermediate colloidal $Fe(OH)_2$ which facilitates subsequent oxidation to the ferric state.

(c) Peroxide Theory - Dunstan, 1905

$Fe + H_2O \rightarrow Fe(OH)_2 + 2H$

$2H + O_2 \rightarrow H_2O_2$

$2Fe(OH)_2 + H_2O_2 \rightarrow 2Fe(OH)_3$

$Fe + H_2O_2 \rightarrow Fe(OH)_2$

(d) Direct Chemical Attack Theory - Bengough and Stuart, 1922

$M + H_2O + 1/2O_2 \rightarrow M(OH)_2$

(e) Biological and Film Theories

(f) Electrochemical Theory - Whitney, 1903 and Walker, 1907

1. Fe(metal) + $2H^+$ (ionic) $\rightarrow$ Fe^{++} (ionic + 2H (atomic)
2. (a) 2H + 1/2 (dissolved) $\rightarrow$ H_2O (liquid water)
   (b) 2H (atomic) $\rightarrow$ H_2 (molecular)

The subject of corrosion is complicated by the enormous number of variables encountered in the two principal factors, the metal and the corroding medium. The methods of protection adopted must vary with the particular combination of these variables encountered.

Generally speaking, when a given metal suffers corrosion under any given set of conditions, two main methods exist of overcoming the difficulty:

(1) Apply a protective coating, or
(2) Replace it with another more resistant metal.

Protective Coatings:

From an electrochemical point of view protective coatings may be considered either anodic or cathodic to the base metal. Anodic and cathodic are often used in such a sense as, iron is anodic to copper, signifying that were the two immersed in a solution of an electrolyte, the iron would act as the anode and go into solution first. Consequently, in the case of a coating that is cathodic to the base metal, any break in the coating will result in localized corrosion (pitting), since the iron base metal will be anodic.

Prior to the application of any protective coating the base metal must be thoroughly cleaned. Various methods are in use,

but the methods of pickling and sandblasting are of prime importance. Acid pickling is carried out in either a dilute sulfuric or hydrochloric acid bath at approximately 80° C°. The process whereby the metallic article is made the cathode in an electrolytic cell is generally known as electrolytic pickling. A second cleaning method which has proved most effective is sandblasting. This process often is used in the field for the preparation of large surfaces for recoating under conditions where pickling and other methods of cleaning are inadequate.

(a) Oxide Coatings:

It is a well-known fact that the high corrosion resistance of reactive aluminum is due to an extremely thin, yet protective, skin of oxide which spontaneously forms on exposure to the atmosphere. Nickel, magnesium and chromium also develop protective oxides and, like aluminum, carry this property with them to their alloys.

The anodic oxidation of aluminum - called "anodizing" - now has found much commercial application. The process consists chiefly in making the aluminum article the anode in a suitable electrolyte. Bengough and Stuart in their original process used a 3% chromic acid bath, but recently the "alumilite" method, using a sulfuric acid bath, has been exploited in the United States. Germany and Japan utilize an oxalic acid bath in a method known as the "Eloxal" process. A very analagous anodic oxidation method has been recently developed for the production of oxides of magnesium, especially in its alloys which find extensive use in air-craft.

(b) Films of Metallic Compounds Other Than Oxides:

The principle of making the corrosion product of the metal protect the metal is made use of with regard to other compounds in addition to the oxides. The most notable examples are the use of phosphate coats on iron, processes known as "coslettizing" and "parkerizing". The principle of each is the production of an iron phosphate skin on the article treated, the variation consisting in the introduction of other metallic phosphates, viz., zinc, copper or manganese.

(c) Coats of Other Metals:

The process whereby one metal is treated with a coat of another is no doubt one of the most important and best-known methods of corrosion protection. Extensive use is made of this method of protection, particularly on steels. The coatings may be applied in the following ways:

1. Simple Metallic Replacement: - This method, although theoretically very simple, finds little application because such coatings are powdery and spongy with little protective value.

2. Electrolytically Depostied Coatings: - In this method the article to be coated is made the cathode in a suitable electrolytic cell. The amount of deposit is proportional to the quantity of current used. Nickel, copper, chromium and zinc find the most extensive use as electrolytically deposited coats, although silver and cadmium are used in specific instances.

3. Hot-Dipping: - The process consists in immersing bodily the article to be coated in a bath of molten metal. Usually nothing additional is done to change the properties of the metal coating which adhere to the surface upon removing the article from the molten metal bath.

a. Tin-plating; Because of its importance in modern economics, tin-plating has been subjected to a great deal of research.

The weight of coating varies from 0.1 oz./sq.ft. to 1.3 oz./sq.ft., corresponding to a coating thickness of 0.00009 to 0.0009 inches. As in case of other coatings, the protective value is somewhat proportional to the thickness. b. Galvanizing; The chief factor controlling the usefulness of the protective layer is the thickness. The coating consists of nearly pure zinc to Zn-Fe alloy in propo tions varied according to the time of immersion in the bath. One particular set of specifications is: Class A - 2.50 oz./sq.ft.; Class B - 2.00; Class C - 1.25. Hot-dip galvanizing finds specific use in case of pipes, steel sheets, and wire. The main disadvantage of galvanizing is the wastage of Zn through the formation of dross (a semi-solid Zn-Fe alloy which settles out in the zinc bath).

4. Metal Spraying: - In this process the metal (usually in the form of a wire) is fed into the gun by a geared air turbine and is reduced to the molten state in the oxy-acetylene cone flame. In this condition the metal is picked up by an air blast, atomized, and in this semi-molten state is driven at a high velocity against the surface of the base metal. Microscopic examination has shown the bond between the surface of the base and the coating to be purely mechanical and of a highly crystalline nature.

5. Powder Treatment: - In the well-known sherardizing process investigators have proved the formation of a Zn-Fe alloy, the action evidently taking place through the vapor phase. A $FeZn_3$ alloy probably forms next to the iron and a $FeZn_7$ alloy (mixed with metallic Zn) farther out. The calorizing process is essentially the sherardizing process applied to aluminum. There is formed, as in the case of zinc, an alloy of the Al with the Fe. A distinct protection advantage in this method is the formation of aluminum oxide in the calorized surface, thus protecting the metal to a large extent from further oxidation.

6. Composite Rolling or Drawing: - Certain pairs of metals may be joined by rolling or drawing bars or ingots of them in contact with one another. Rolled gold is probably the oldest example of this technique, but copper-clad and nickel-clad steel and alclad duralumin are modern examples of the same art. Coatings such as these would appear to be less likely to suffer from porosity then the older types already described.

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Reported by
R. C. Gunther
November 28,1939

Inorganic Seminar December 12, 1939

I LEAD SUB-OXIDE
II THE DIMETHYL PHOSPHATES OF THE RARE-EARTH METALS
III DEUTERIUM PEROXIDE

I

Much conflicting evidence has been obtained with regard to the existence of lead sub-oxide, Pb_2O.

Accurate analyses of the gases evolved when lead oxalate was decomposed in a vacuum at low temperatures (about 300°C) and X-ray analyses and approximate determination of the electrical conductivity of the residue suggest that the grey-black powder obtained is really an intimate mixture of lead and lead monoxide (red tetragonal form) instead of lead sub-oxide as reported by some investigators. The reaction is (1) instead of (2).

$$(1)\ 3Pb(O.OC)_2 \xrightarrow[\Delta]{300^\circ} 2PbO + Pb + 4CO_2 + 2CO$$
(66.6% of gases is CO_2)

$$(2)\ 2Pb(O.OC)_2 \xrightarrow[\Delta]{300^\circ} Pb_2O + 3CO_2 + CO$$
(75% of gases is CO_2)

II

The great range, the higher rate of change in the yttrium group than in the cerium group and the great decrease in solubility with rise in temperature are noteworthy features of the dimethyl phosphates. They are of practical utility for the purification of terbium, dysprosium and holmium.

The solubility falls steadily from lanthanum to lutecium. The negative temperature coefficient is remarkably high especially as the atomic number increases. There is a proportional increase in this coefficient as the solubility of the dimethyl phosphates decreases or as the atomic number increases. But in practice the final temperatures of crystallization were kept below 50°C to prevent serious hydrolysis of the salts. With the exceptions of La and Ce the salts are anhydrous. The very small solubilities of the dimethyl phosphates of erbium or rare-earth metals of higher atomic number together with a greater ease of hydrolysis make them unsuitable for fractional crystallization. Terbium, dysprosium and holmium should be concentrated to a reasonable degree before use of dimethyl phosphates.

Crude yttrium earths were fractionated as bromates till Tb, Dy, Ho and Y were removed (4000 crystallizations). Ho and Y were partially separated by the basic nitrite method. Then the dimethyl phosphate method was used. The dimethyl phosphate was made by Schiff's method.

$$POCl_3 + 3CH_3OH \xrightarrow{\text{below } 30^\circ} (CH_3)_2HPO_4 + 3HCl + CH_3Cl$$

70 fractions and 55 series of crystallizations were made.

<u>Terbium</u>. It contained less then 1 part of Dy in 1100 parts
" " " " 1 part of Gd in 1000 parts

<u>Dysprosium</u>. 99.9% pure Dy was obtained. It contained some Gb and Tb which colored it a light tan.

<u>Holmium</u>. 99% pure Ho was obtained with about 1% Dy. No Y was present.

D_2SO_4. It was made by subliming SO_3 and dissolving it in D_2O.

D_2O_2. D_2O vapor was passed under vacuum thru a mixture of D_2SO_4, D_2O and $K_2S_2O_8$ which was held at 70-90°C. The arising vapor of D_2O and D_2O_2 was fractionally condensed to condense the D_2O_2. The vapor which was not condensed was recirculated several times. Then the D_2O_2 was concentrated.

HDO_2. From the equation

$$H_2O_2 + D_2O_2 \rightleftharpoons HDO_2 \qquad K=3.3 \text{ or } 4$$

the greatest concentration of HDO_2 would be about 50%.

Recovery of D_2O and D_2SO_4 From the Apparatus. After standing a few days to decompose the D_2O_2 the contents of the reaction flask were distilled under vacuum. The excess D_2O, D_2SO_4 and D_2O came over in the order given, the second distillation of D_2O coming from the decomposition of $KDSO_4$

$$2KDSO_4 \xrightarrow[\Delta]{} K_2S_2O_7 + D_2O$$

References:

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Other references are given in each of these three references.

Reported by
Hugh W. Stewart

Inorganic Seminar January 9, 1940

THE USE OF ARTIFICIAL RADIOACTIVE ISOTOPES AS INDICATORS

Naturally occurring radioactive elements have been used as indicators in determining solubility of salts of radioelements and the corresponding inactive isotopes, in measuring surface area of and adsorption on finely divided material, and in finding evidence for the existence of compounds, as was done with bismuth hydride. The usefulness of naturally occurring radioelements as means for acquiring information on reaction mechanism or physical constants is slight, since so few of the elements are naturally radioactive. This handicap has been overcome by the advent of artificial radioactive elements--radioactive elements produced by bombardment of atoms of an element or a neighboring element with some elementary particle. The common bombarding particles are neutrons (from a beryllium-radium mixture or from a deuteron-deuteron disintegration), deuterons, protons, and alpha particles. All elements except two or three can be produced in radioactive form, and many have sufficiently long half lives for use in investigations.

The common technique is to concentrate the radioactive element by simple chemical means, after the addition of some of the inactive element as a carrier. It would be better to concentrate the active isotope by itself, as has been done in a few instances, but this procedure has not been developed for many elements and would not furnish large enough amounts of material for synthesis.

The short half-lives of these isotopes requires that the all syntheses and interchange reactions be carried out in a short time. The most useful and most easily interpreted reaction is an exchange reaction. Two compounds are allowed to react in solution and are then separately examined for activity. The mechanism of a reaction or the stability of a compound can be decided from the action of the radioactive isotope, i. e. whether the active isotope in one compound exchanges with the corresponding inactive isotope in the other.

Since the activity of these isotopes is small, it must be determined with a sensitive electroscope, or, better, by a Geiger-Müller counter with amplifier and scaling circuit. The material which is being investigated is spread in a thin layer and then examined. The change in activity of the two compounds is a measure of the interchange. The activity is compared with a decay curve of the isotope or with the activity of an untreated active material.

The varied problems which can be attacked by this means and the technique of this work are best shown by the following examples from the literature.

<u>Isomerism of $(Coen_2Cl_2)Cl$:</u> "It has long been known that green 1:6 $(Coen_2Cl_2)Cl$ changes into the violet 1:2 salt on evaporation of the aqueous solution to dryness, and that the reverse transformation is promoted by hydrochloric acid. The mechanism of interconversion has remained a matter of conjecture. Investigation of the redistribution of component chlorine atoms during isomerization with the aid of radiochloride has assisted in clarifying the problem. Interchange of nuclear and ionic chlorine was necessary for isomerization, so intramolecular rearrangement can be disregarded. The immediate result of dissolving the compounds in hot water is the replacement of chloride ion by water within the coordination spheres; the original complex ions are reformed on concentration of the solution by evaporation. The relative amounts of the isomeric chlorides in the solid residue appear to be largely controlled by solubility considerations. The cis-

chloride is less soluble than the trans-; but the latter alone forms a sparingly soluble addition compound with hydrochloric acid. Apart from its function as a precipitant, hydrochloric acid plays no essential role in the cis-trans change."

Racemization of $K_3(Cr(C_2O_4)_3)$: $(Cr(C_2O_4)_3)^{---}$ can be resolved to give optically active forms which racemize readily in aqeuous solution. It has been supposed that the chromoxalate ion dissociates and the products recombine to give the racemic mixture

$$(Cr(C_2O_4)_3)^{---} \rightleftharpoons (Cr(C_2O_4)_2)^{-} + C_2O_4^{--}$$

However, when potassium chromioxalate solutions were treated with oxalated ion containing radioactive carbon, no interchange of oxalate ion occurred. This indicates that there is an intramolecular rearrangement rather than an ionization.

Exchange Reactions of Sulfur: 1. Polysulfide: Sulfur atoms in polysulfide would be expected to interchange and this was found. Active sulfur was dissolved in ammonium sulfide. The hydrogen sulfide which could be liberated from the polysulfide by acid was active. This indicates the change $(HSS^*)^- \rightleftharpoons (HS^*S)^-$. It was found to be rapid.

2. Sulfide-Thiosulfate: When a solution of active sodium sulfide and sodium thiosulfate were heated at 100° for several hours, an interchange occurred, resulting in the formation of an active thiosulfate. There are two possible mechanisms

1. a direct interchange

$$HS^{*-} + SSO_3^{--} \rightleftharpoons HS^- + S^*SO_3^{--}$$

(analogous to $O^{18}H^- + PO_4^{---} \rightleftharpoons O^{16}H^- + PO_3O^{18}{}^{---}$

or 2.

$$S_2O_3^{--} \rightleftharpoons S + SO_3^{--}$$

$$S + S^{*--} \rightleftharpoons SS^{*--} \rightleftharpoons S^* + S^{--}$$

$$S^* + SO_3^{--} \rightleftharpoons S^*SO_3^{--}$$

The interchange is slow and appears to follow mehcnism 1.

3. Sulfite-Thiosulfate: $S^*O_3^{--} + S_2O_3^{--} \rightleftharpoons SS^*O_3^{--} + SO_3^{--}$

This is a rapid reaction. The high speed of this interchange and the polysulfide interchange makes the second possibility of the previous exchange unlikely:

4. Sulfide-Sulfate: No interchange occurs. This is in harmony with the generalization that complex ions in different states of oxidation do not interchange the central atoms. In the case of phosphate-hypophosphite no interchange of phosphorus atoms occurs.

5. Sulfite-Sulfate: No interchang, for a similar reason.

6. Sulfur Dioxide -Sulfur Trioxide: When active suflur trioxide was heated with sulfur dioxide, exchange took place only at a temperature at which dissociation of sulfur trioxide occurs

$$SO_2 + S^*O_3 \rightleftharpoons SO_2 + 1/2O_2 + S^*O_2 \rightleftharpoons SO_3 + S^*O_2$$

Halogen-Halide ion Exchange: An active halide ion (fluorine has not been tried) when treated with the halogen yields the active halogen at a rate greater than the hydrolysis of the halogen. The mechanism is probably $X^{*-} + X_2 \rightleftharpoons X_3^- \rightleftharpoons X^- + XX^*$. The interchange between different halides and halogens has not been tried.

Miscellaneous: The diffusion of a layer of long-lived active isotope as metal into the metal has been measured in the case of copper and gold.

Impurities in an element or compound can be detected and estimated by means of the decay curves of a specimen that has been irradiated with neutrons or deuterons.

The chemistry of elements that have not been isolated from natural sources can be approximated by the study of artificially produced active forms of the elements. This has been done for element 43 and the trans-uranium elements.

It can be seen from these few examples that the use of artificial radioactive isotopes can shed much light on reaction that would be difficult to analyzie in any other way. There is much that can be solved with the aid of these labelled atoms.

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Reported by Eugene O. Brimm

Cl^{17} — Cl^{18}
Mn^{25} — Mn^{26}

INORGANIC SEMINAR February 27 1940

ADDITION PRODUCTS OF BF_3 WITH SULPHATES AND PHOSPHATES

Electronic considerations:

BF_3 is similar to SO_3 in several respects. Both form addition products with organic and inorganic compounds. This similarity is explained on the basis of electron configurations, since both compounds have an incomplete octet.

Reactions with sulphates:

SO_3 adds to K_2SO_4 to give the pyrosulphate $K_2S_2O_7$. A similar reaction occurs with BF_3. However, under proper conditions two molecules of boronfluoride can be added.

The same reaction can be run with cesium, lithium or sodium sulphate, but the rates of reaction differ. They seem to depend on the atomic weight and diameter. Alkali earth sulfates are indifferent to BF_3.

Newly formed compounds are addition compounds; on heating BF_3 is evolved, and can be quantitatively recovered. When dissolved in water HBF_4 and HBO_2 are formed.

Reaction with phosphates:

$$9SO_3 + 2K_3PO_4 \text{ -- } 3K_2S_3O_{10} + P_2O_5$$

However, boron trifluoride reacts with phosphates to form addition compounds. Proof of this reaction lies in the fact that the temperature of reaction, any P_2O_5 formed would be volatilized and that the solution of this compound still shows test for phosphate. This could not occur if the reaction went:

$$4K_3PO_4 + 12\ BF_3 \text{ -- } 2P_2O_5 + 9KBF_4 + 3KBO_2$$

Both reactions are carried out by passing dry BF_3 over the salt, in a tube which may be heated.

REACTION OF BF_3 WITH BORATES, BORON TRIOXIDE, CARBONATES AND NITRATES

BF_3 seems to drive B_2O_3 from a borate. The gas formed decomposes when it strikes a cold surface. It has been postulated that the substance formed is a trimer of BO_4.

The structure has been proposed as one resembling benzene. The deposit contains fluorine and oxygen, and is a compound of B_2O_3 with BF_3 in the ratio of 3:1, or 2: 1.

BF_3 reacts with salts which are easily decomposed to form $(BOF)_3$ The effect has also been noticed on oxides.

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Peter M. Barneys

Inorganic Seminar February 27, [illegible]

Thionyl Chloride

Thionyl chloride has long been recognized as a valuable reagent, and its use has greatly increased recently due to the greater ease with which it is now prepared.

Historical:

Kremer (1), in 1849, passed dry SO_2 over PCl_5 and obtained a greenish liquid to which he assigned the formula $PCl_5.2SO_2$. This was probably a mixture of $POCl_3$ and $SOCl_2$. In 1857, Hugo Schiff (2) prepared $SOCl_2$ from Kremer's product by a careful fractional distillation. His product boiled at 82° C. To Schiff goes the credit of being the first to prepare thionyl chloride. Carius was probably the first to investigate thionyl chloride very extensively. He prepared it by the action of $POCl_3$ on $CaSO_3$.

Physical Properties:

Thionyl chloride is a colorless, refractive liquid which fumes in air. It has a very penetrating odor similar to sulfur dioxide. The specific gravity is 1.6767 at 0°C.; melting point is -104°; boiling point is 78.8°. The theoretical molecular weight of thionyl chloride is 119. The molecular weight in boiling chloroform is 229-235 and in freezing benzene, it is 108-110.

Methods of preparation:

Silberrad (3) reports three practical methods for preparing thionyl chloride:

1) Action of sulfur dioxide on phosphorus pentachloride:

$$SO_2 + PCl_5 \rightarrow POCl_3 + SOCl_2$$

A later modification was: $PCl_3 + SO_2Cl_2 \rightarrow POCl_3 + SOCl_2$

These have largely been superseded.

2) Interaction of a chloride of sulfur and sulfur trioxide:

$$S_2Cl_2 + SO_3 \rightarrow SOCl_2 + SO_2 + S$$

The temperature is maintained at 75-80° and a continuous stream of chlorine is passed in to reconvert the sulfur into the monochloride. The yield is almost theoretical.

This reaction was modified later. It is carried out at room temperature in presence of $SbCl_3$ or $HgCl_2$. Either SO_3 or $ClSO_3H$ and SCl_2 or $Cl_2 + S_2Cl_2$ or S may be used.

3) Interaction of phosgene and sulfur dioxide: (most recent method in 1926). When phosgene and sulfur dioxide are passed over wood charcoal at a temperature above 200°, two reactions result:

1) $COCl_2 + SO_2 \rightarrow SOCl_2 + CO_2$

2) $2COCl_2 + SO_2 \rightarrow SCl_4 + 2CO_2$

Reaction 1 predominates at lower temperature and with an excess of sulfur dioxide. The phosgene may be replaced by a mixture of carbon monoxide and either chlorine or sulfuryl chloride.

Since Silberrad's review in 1926, only two other methods have been described in the literature:

1) Patent by Elko Chemcial Co. for the production of $SOCl_2$ and $POCl_3$ (4)

$$2P + 2SO_2 + 5Cl_2 \rightarrow 2SOCl_2 + 2POCl_3$$

2) Patent by Hooker Electrochemical Co. (5). Sulfuric acid is treated with sulfur dichloride and chlorine. The thionyl chloride formed is removed by distillation.

Reactions of Thionyl Chloride:

A. With Inorganic Compounds:

Thionyl chloride is an extremely reactive reagent, effecting both chlorination and reduction. The chlorine almost always appears in combination with the substance acted upon while the sulfur appears in combination with either oxygen or chlorine. Thionyl chloride boils without decomposition, but at 440° is completely dissociated corresponding to the equation:

$$4\ SOCl_2 \rightarrow S_2Cl_2 + 2SO_2 + 3Cl_2$$

It reacts vigorously with water with the evolution of HCl and SO_2 (other products are reported). Most elements are attacked with the formation of chlorides. Many metallic oxides are also converted into chlorides: $MS + 2SOCl_2 \rightarrow MCl_2 + SO_2 + S_2Cl_2$.

It reacts with ammonia to form nitrogen sulfide (N_4S_4), and ammonium chloride, sulfite, and polythionates. It reacts vigorously with nickel carbonyl to form NiCl with an evolution of SO_2 and CO: $2Ni(CO)_4 + 2SOCl_2 \rightarrow 2NiCl + SO_2 + 8CO + S$ (fall in temperature). If dry HBr is passed in, thionyl bromide is formed.

$$SOCl_2 + 2HBr \rightarrow SOBr_2 + 2HCl$$

B. With Organic Compounds

The chief importance of thionyl chloride is its use in Organic Chemistry. Its reaction with organic compounds have been classified by Silberrad as follows:

1. Introduction of chlorine in place of various groups, e.g. OH, SH, NO_2, SO_3H; or of hydrogen or oxygen.
2. Introduction of sulfur, alone or in combiatnion with oxygen to form the thionyl group.
3. Dehydration.
4. Removal of hydrogen
5. Condensations not included in the foregoing
6. Catalytic action

The reactions will be taken up in brief under the above headings

1) The replacement of hydroxyl by chlorine is the most frequently occurring and important reaction of thionyl chloride. Many alcohols can be converted into chlorides. This is a very general reaction for the conversion of carboxyllic acids into acid chlorides. Many aromatic nitro compounds can be converted into the corresponding chloro derivatives; the same is true for aromatic sulfonic acids or their salts. Some aldehydes can be converted to the dichloride by replacement of the oxygen.

Many ethers react with thionyl chloride in the presence of $SnCl_4$ or $TiCl_4$ to form chlorides:

$$SOCl_2 + Et_2O \rightarrow 2EtCl + SO_2 \text{ (good yield)}$$

2)a)Formation of sulfurous esters: $2EtOH + SOCl_2 \rightarrow EtOSOEt$. Phenols will also do this in the presence of CS_2

b)Formation of sulfoxides in the presence of $AlCl_3$ by aromatic compounds.

$$2C_2H_6 + SOCl_2 \rightarrow C_6H_5\text{-}SO\text{-}C_6H_5$$

c)Replacement of hydrogen with sulfur: This occurs with many phenols, leading to the formation of sulfides or sulfenium compounds.

3) Dehydration:

a) Many acids (usually the silver salts) form anhydrides.

b) Acid amides and aldoximes are converted to nitriles.

4) Removal of hydrogen:
Some mercaptans react to form polysulfides
$4EtSH + SOCl_2 \rightarrow Et_2S_2 + Et_2S_2 + Et_2S_3 + H_2O + 2HCl$

5) Some condensations not already mentioned. Under special conditions: $3C_6H_5\text{-}OH + SOCl_2 \rightarrow (C_6H_4\text{-}OH)_3SC + HCl + H_2O$

6) Catalytic action:
Certain Friedel-Crafts reactions are accelerated
It is active in many Walden inversions

The reactions of thionyl chloride with phenols are rather interesting:
a) The two react alone in the cold to form $S(C_6H_4\text{-}OH)_2$ and some resins.
b) If dissolved in CS_2 and a little pyridine added, the result is phenyl sulfite
c) If two moles of $SOCl_2$ and three moles of phenol are mixed at 0° and $AlCl_3$ added, the main reaction is:
$3C_6H_5\text{-}OH + SOCl_2 \rightarrow (C_6H_4\text{-}OH)_3SCl + HCl + H_2O$
d) If one mole of $SOCl_2$ is added to a mixture of an equal weight of $AlCl_3$ and two moles of phenol in CS_2 at 0°, the reaction is:
$2C_6H_5OH + SOCl_2 \rightarrow (C_6H_4\text{-}OH)_2SO + 2HCl$

The most frequent use of thionyl chloride is the conversion of acid into its chloride. This reaction is becoming more and more general. This method is more convenient and usually more satisfactory than in the use of phosphorus pentachloride.

The general reaction for the formation of the acid chloride is:
$R\text{-}COOH + SOCl_2 \rightarrow R\text{-}COCl + SO_2 + HCl$
Although the method is very general, there are some acids that will not react. Some examples of acids which will not react to the ordinary procedure are oxalic acid, p-bromobenzoic, p-hydroxybenzoic, and 3-pyridine carboxylic acids. The reaction usually will not work with ketonic acids. In general, a negative group such as NO_2 or Br in the para position inhibits the formation of the chloride: p-hydroxy acids will not react; acids which easily form the anhydride yield this instead of the chloride; silver salts of acids usually give the anhydrides.

It has recently been found that pyridine facilitates the formation of the acid chlorides of compounds which react with difficulty (6) For example, p-nitrobenzoic and p-bromobenzoic acids in ether or chloroform will give the chloride with $SOCl_2$ in the presence of pyridine.

The present price of thionyl chloride is about fifty cents per pound. Eastman Kodak quotes $2.50 per kilo in small lots. The Hooker Co. is now manufacturing it by the method described in their patent.

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Stanley B. Speck

$Cr\,Cr\,O_4$

$Cr_2(CrO_4)_3 = Cr_5O_{12}$

INORGANIC SEMINAR

March 5, 1940

NITROSYL CHLORIDE

Introduction.

Since nitrosyl chloride is one of the active components of aqua regio (1)(7)(20) we can consider the compound as one of the oldest laboratory chemicals known

$$HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O$$

Properties

Nitrosyl chloride is a red to red yellow liquid with a chlorine like suffocating odor. It melts at -61° and vaporizes at -5.8°; it is not associated in the liquid or in the vapor state (2)(3). Irradiation by light of 4400 to 5200 Å brings about a partial dissociation (4)

$$h\nu + NOCl \rightarrow NO + Cl$$
$$Cl + Cl \rightarrow Cl_2$$

at 6270° Å reformation of the NOCl takes place from the NO and Cl_2(5).

Preparation.

I Tilden (6) proposed the following

$$NOCl + SO_2(OH)_2 \rightarrow SO_2(OH).O.NO + HCl$$
$$NaCl + SO_2(OH)ONO \rightarrow SO_2(OH)ONa + NOCl$$

as a method for preparing the pure nitrosyl chloride. Sulfuric acid was saturated with the vapors from aqua regia, salt was then added liberating NOCl free from hydrogen chloride. Tilden has proposed the monochloride as the only true chemical compound of nitric oxide and chlorine generated from a mixture of nitric and hydrochloric acids.

II The above conclusions of Tilden were utilized by Briner and Pylkoff (7)(8)(3) for preparing NOCl by direct union of nitric oxide and chlorine.

$$2\ NO + Cl_2 \rightarrow 2NOCl$$

The reaction proceeds at all temperatures between 8 and 290° following a third order reaction (9). Equilibrium is quickly established between NO, Cl_2, and NOCl at 450 to 600° A. The following mechanism has been proposed for the reaction:

$$\underline{I}\quad NO + Cl_2 \rightarrow NOCl_2$$
$$\underline{II}\quad NOCl_2 + NO \rightarrow 2NOCl$$

Strong evidence is found for I since in studying the cooling curve of NOCl-Cl_2 system a definite halt point exists at the composition point corresponding to $NOCl_2$.

Much confusion is found in the literature with respect to catalytic effects. Trautz and Henglein (10) reported no effect on the reaction by surfaces or the presence of paraffin or graphite. Francesconi and Bresciani (12) reported an increase in the reaction rate but no increase in yield by the use of charcoal. Kiss (11) verified this by showing that rough surfaced tend to catalize the reaction. He reported also the use of small amounts of bromide which apparently forms NOBr, giving NOCl on subsequent reaction with Cl_2.

III. Whittaker, Lundstron and Merz found that the free energy relationships (13) favored the reaction between nitrogen dioxide and potassium chloride. A by product proved to be nitrosyl chloride

$$KCl + 2NO_2 \rightarrow KNO_3 + NOCl$$

Without the presence of a small amount of water the reaction goes to only a few per cent.

IV. Skinner (14), desiring a more practical laboratory method whereby nitrosyl chloride could be made quickly, conveniently,

and reasonably pure, modified a procedure proposed by Naquet (22)

$$NaNO_2 + PCl_5 \rightarrow NaCl + POCl_3 + NOCl$$

Instead of using the solid PCl_5, Skinner used the oxychloride. Experimentally the $POCl_3$ is added dropwise to sodium nitrite. After a period of several minutes the red gaseous NOCl is evolved and is drawn thru a suitable train for the removal of contaminating $POCl_3$. The reaction mixture must be continually agitated to prevent solidification. Even with this precaution the reaction stops after 50% of the theoretical amount of NOCl is liberated. Dry nitrogen is passed thru the train before starting the reaction to insure a dry system. The nitrosyl chloride is condensed in a suitable apparatus immersed either in acetone and CO_2, or in ice and concentrated brine. The product can then be distilled into small preweighed capillary neck ampules, sealed and stored for subsequent analysis. Three types of analyses were carried out:

1. The ampules were broken under alkali in a closed system and the excess alkali titrated
2. The available chlorine was titrated
3. An attempt was made to test the purity by use of sulfamic acid which liberates nitrogen quantitatively from nitrites.

$$NH_2SO_3H + NaNO_2 \rightarrow NaHSO_4 + N_2 + H_2O$$

The results were low by some 5%. This is explained by the fact (15) that some nitric oxide is formed thus giving rise to nitrate. The nitrate is unaffected by sulfamic acid.

A possible reason for the incomplete reaction may be the formation of a rather stable addition product between $POCl_3$ and nitrite, or one of the products of the reaction. Analysis of the reaction residue shows that meta phosphate must be formed.

V $2NaNO_2 + POCl_3 \rightarrow 2NOCl + NaPO_3 + NaCl$

$3NO \rightarrow N_2O_3 + 1/2\ N_2$

$N_2O_3 + 2HCl \rightarrow 2NOCl + H_2O$

At ordinary temperatures and pressure of 500 to 1000 atm.(16)

VI $NO + FeCl_3 \rightarrow NOCl + FeCl_2$

At sublimation temperature of $FeCl_3$ (17)

VII $NO_2 + PCl_5 \rightarrow NOCl + 1/2Cl_2 + POCl_3$

Gaseous NO_2 introduced into cooled PCl_5 (18)

VIII $2NO_2 + Cl_2 \rightarrow 2NO_2Cl$

$NO_2Cl + NO \rightarrow NOCl + NO_2$

Thus proposing NO_2Cl as an intermediate. The reaction proceeds at 18° as a second order reaction, catalized by white light, diffused daylight and moisture.

<u>Reactions:</u>

1 With elements

H_2 -- explodes with equal parts when catalized by Pd. NOCl is reduced to N_2.

K -- not attacked in cold, but burns vigorously when heated

Ag --when finely pulverized will react. Scott and Johnson (23) utilized the affinity of NOCl for Ag to find the Ag:NOCl ratio and thus the atomic weight of chlorine. NOCl for this purpose was prepared by the method by Pylkoff (3).

Au--reacts

Hg--gives $HgCl_2$

Al--no reaction

Cl_2--probably forms a series of addition compounds.

2. With acids

Sulfuric acid - Chlorine and HCl are evolved and the acid turns yellow

Hydrosulfuric acid--In an inert solvent NOCl is reduced to NH_4Cl

3. With bases.

Sodium hydroxide - Sodium chloride and nitrite are the chief constituents. Badurimont (20) reported the products as being chloride and nitrate which does not check with present work.

4. With salts.

In general an addition takes place, however an interesting reaction is found with silver bisulfate

$$SO_2 \begin{matrix} OAg \\ OH \end{matrix} + NOCl \longrightarrow SO_2 \begin{matrix} ONO \\ OH \end{matrix} + AgCl$$

5. Addition compounds

Various substances form addition compounds with NOCl. The reactions are usually carried out below -10° by bringing the halide in contact with the liquid. Sudborough (21) found some addition compounds to form at higher temperatures. There is some doubt as to the structure of the compounds as is illustrated by the possibilities for $SnCl_4.2NOCl$

$$(1)\ Cl_4Sn \begin{matrix} O{:}N.Cl \\ O{:}N{:}Cl \end{matrix} \qquad (2)\ Cl_4Sn \begin{matrix} Cl.N{:}O \\ Cl.N{:}O \end{matrix} \qquad (3)\ \left[SnCl_6\right](NO)_2$$

A few others may be noted to show that their formation is not limited with regard to the position of the element in the periodic chart. The characteristic color is yellow or orange; however, several of the compounds of the first group metals are dark brown or black.

Cu -- $Cu_2Cl_2.2NOCl$

or $\begin{matrix} (Hg_2Cl_2 \\ (HgCl_2 \end{matrix}$ -- $HgCl_2.NOCl$

BCl_3 -- $BCl_3.NOCl$

$TiCl_2$ - $3TiCl_2.2NOCl$

$TiCl_4$ -- $TiCl_4.2NOCl$

$Pb + SnCl_4$ -- $PbCl_4.2NOCl$
$SnCl_4.2NOCl$

Fe -- $FeCl_2.NOCl$

$FeCl_2$ - $FeCl_2.NOCl$

$PtCl_4$ -- $PtCl_4.2NOCl$

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Robert C. Brasted

COMPOUNDS OF THE RARE GASES

I. Early work
   A. Fischer and Schroter could form no compounds by arcing 45 different metals under liquid Argon, (1910)
   B. Skaupy theorized that a noble gas could share an outer electron to complete the shell of an element such as chlorine (1920)

II. Reactions of inert gases with elements under temporary excited conditions.
   A. Helium hydride
      1. Is it a molecule or ion?
   B. Non-metal helides
      1. Boomer formed helides of I, S, and P. (1925)
      2. Antropoff and co-workers passed A and KR, mixed with Cl and Br, through discharge tubes. They isolated a red solid, stable at room temperatures for several days. It was later shown to be a compound of NO and HCl. (1932)
   C. Metal helides
      1. Manley: Hg helide. (1924)
      2. Boomer: Hg and W helides. (1925)
      3. Morrison: Bi helide. (1927)
      4. Krefft and Rompe: Compounds of Tl, In, Zn, Na, K, and Rb with Ne, A, and He. (1931)
      5. Damianovich: Compounds of Pt, Pd, Fe, Bi, Na, and U with He and of Pt with A and Xe. (1929-date)
   D. Conclusions
      1. Excited or disrupted inert gas atoms may unite in true chemical fashion with other elements
      2. Adsorption of the gases doubtless occurs also, - hence variable and fractional molecular formulas.

III. Compounds formed by coordinate link of inert gas atoms with molecules containing an incomplete octet
   A. Hydrates
      1. Argon, by Villard. (1896)
         a. Dissociation pressure of 105 atmospheres at 0° C.
      2. Krypton, by de Forcrand. (1923)
         a. Dissociation pressure of 98.5 atmospheres at 0.2° C.
      3. Xenon, by de Forcrand. (1925)
         a. Dissociation pressure of 1.15 atmospheres at 0.2° C.
         b. No Neon hydrate under 260 atmospheres pressure
      4. Radon, by Nikitin. (1936)
         a. Dissociation pressure of one atmosphere at 0° C.
         b. Formula, $Rn.6H_2O$
         c. Similar formulas for other rare gas hydrates
   B. "Deuterates", by Calas (1936)
      1. $Kr.6D_2O$, with dissociation pressure of one atmosphere at -25°C
      2. $Xe.6D_2O$, with dissociation pressure of one atmosphere at -3°C
   C. Boron trifluoride addition compounds, by Booth. (1935)
      1. $A.BF_3$, $A.2BF_3$, $A.3BF_3$, $A.6BF_3$, $A.8BF_3$, $A.16BF_3$
      2. Stable only from -130 to -127° C.

IV. Separation of rare gases by variations in "chemical activity."
   A. Due to the wide range of the dissociation pressures of the hydrates listed, it should be theoretically possible to separate the gases on this chemical basis.
   B. Nikitin found this separation possible. It was more efficient if the hydrates were deposited in the presence of a large

excess of $SO_2.6H_2O$ crystals, with which they are isomorphous. Radon and Argon are easily separated from the other gases, but more difficultly from each other.

C. Nikitin made the interesting observation that Radon and Argon resemble each other in chemical properties much more than they do their neighboring gases in the periodic table.

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J. B. Work

INORGANIC SEMINAR March 18, 1 0

OXIDES AND OXYACIDS OF FLUORINE

I. HISTORY:

Lebeau and Daminens (1) in 1929, electrolyzed KHF_2 and passed the fluorine into a 2% sodium hydroxide solution. They obtained a gaseous mixture which was thought to consist mainly of oxygen, and an oxide of fluorine(F_2O). Fractional distillation from a liquid air bath yielded a substance whose analysis approached F_2O 97% pure. bp - 167°. d(-166°) = 1.835

$$2NaOH + 2F_2 \rightarrow 2NaF + F_2O + H_2O$$

This was the first reported fluorine oxide. Since 1929, the confirmation of the existence of F_2O, and the discovery of F_2O_2 have been reported. The radical FO has been reported but it appears doubtful that it actually exists.

II. DIFLUOROOXIDE: F_2O

A. Preparation:

$$Fe + 2H_2O \xrightarrow{0°} (H_2O_2) + F_2O$$

$$F_2 + \text{cold aqueous } NaOH, KOH, Ca(OH)_2 \rightarrow F_2O + MF + O_2$$

The reaction with water is said to yield ozone, ozonates, and hydrogen peroxide (2). Ruff (3) prepared 99.8% F_2O by this method. The crude oxide is liquefied in liquid air bath, and fractionally distilled in quartz, apparatus at reduced pressures. The impurity was identified as CF_4, by bp, density, and non-reaction with NaOH and HI. Some C_2F_6 and SO_2F_2 were produced; the latter due to the presence of sulfate in the technical KHF_2. However, the method of analysis of F_2O, absorption in HI and titration of the iodine released, was later (6) shown to be inaccurate.

Several other reactions have been reported in which F_2O is produced:

$$F_2 + CO_2 + H_2O \rightarrow O_2 + F_2O \quad \underline{4} \quad + 7.$$

$$NO_3F + H_2O \xrightarrow{\underline{5}} F_2O + O_2 + HF + HNO_3$$

B. Properties

1. Physical:

At room temperature it is a colorless stable (7) gas. It has bp.-144.8°, mp-223.8° d(-165°)=1.65. Grave physiological effects result when inhaled, even more so than for fluorine.

The O-F bond angel (105 ±5) and atomic distances (14.Å) have been measured (8). 100 cc. of water at 0° dissolve 6.8 C. C. F_2O.

2. Chemical:

<u>In general</u>, F_2O is less reactive than fluorine. Under anhydrous conditions fluorination takes place; in the presence of water, oxidation results. It does not attack glass in the cold.

<u>Reactions with the elements:</u>

Group I A $\xrightarrow[400°]{\text{reflected light}}$ $F_2 + M_2O$ (This is a quantitative reaction)

Group I B ------> colored cpds. --- Cu^{++}, Ag_2F_2, Au^{+++}

Group II B $\xrightarrow{OH}$ MF_2, Hg_2F_2 (at op. of Hg)

Group V

P(red) -- spontaneous reaction --> POF_3, PF_5

As, Sb --> AsF_5

Reactions with compounds:

At room temperature, F_2O is stable to water. However, there is some reaction in presence of water vapor (3,7). Its thermal decomposition has been studied (9, 3). Even at 300° decomposition is not complete.

$$F_2O + H_2O \rightarrow 2HF + 2[O] \rightarrow 2HF + O_2;\ 2F_2O \rightarrow 2F_2 + O_2$$

EXAMPLES:

Anhydrous conditions:

$NaCl \rightarrow NaI + Cl_2$

$Na_2CO_3 \rightarrow NaF + CO_2 + O_2$

$NaNO_3 \rightarrow NaF$ + nitrous gases

glass $\xrightarrow[\text{burns}]{DH}$ SiF_4

PbO --> PbO_2 (This appears to be an exception in that fluorination does not take place)

SO at $\xrightarrow{\text{low T}}$ $(SO_3)_2$

Aqueous solutions:

$AgNO_3 \rightarrow Ag_2O_2$

$4HI + F_2O \xrightarrow[\text{quant.}]{H^+} 2I_2 + 2HF + H_2O$

$NaAsO_2 + F_2O \xrightarrow{?} Na_3AsO_4$

$Cr^{+3} \xrightarrow[OH]{OH-} CrO_4^{=}$

III. DIFLUORO DIOXIDE

Ruff (10) subjected a mixture of one mole of fluorine and one mole of oxygen, cooled in liquid air, to a brush discharge at 30 mm. The apparatus was quartz throughout. The liquid mixutre was then distilled.

Fraction A.	bp. 380 m.	-190°
Fraction B.	bp.	-112° (ozone)
Fraction C.		-- 95° (SiF_4)
Fraction D.		residue (F_2O_2)

The residue was an orange solid, mp-163°, yielding a red liuqid bp-57°., sp. gr. at -87° of 1.533. It analyzed for F_2O_2. Ruff measured the vp at various temperatures and found that decomposition apparently took place according to the following equation:

$$F_2O_2 \rightarrow 2FO \rightarrow 2F + 2O \text{ -- } F_2O_2$$

Later (6) it was shown that FO does not exist. Absorption spectra, bp mp measurements showed that the supposed FO really consisted of a 50-50 mixture of O_2 and F_2.

F_2O_2 is rather unstable, decomposing irreversibly into F_2 and O_2 even at -100°.

At -57°, the reaction is complete. The kinetics of the decomposition have been thoroughly studied by Frisch and Schumacher (6).

The following reaction is quantitative:

$$F_2O_2 + 6HI \rightarrow 2HF + 2H_2O + 3I_2$$

IV. MONOFLUOROOXIDE: - FO

Ruff supposedly prepared this oxide, but a 50-50 mixture of F_2 and O_2 exhibited all the properties of this oxide. Frisch and Schumacher disproved the existence of FO.

V. HIGHER OXIDES:

Higher oxides are theoretically possible, such as F_4O. Analysis of residues from the preparation of F_2O failed to reveal any higher oxides. Attempts to prepare them by passage of F_2 and O_2 through an electric spark failed.

VI. OXYACIDS OF FLUORINE:

No oxy acid or salts of the oxyacids have been isolated and identified (11). However, when F_2 is passed into 50% potassium hydroxide solution at -50°, and the solution then evaporated, the resulting salt has marked oxidizing power. This is thought to be due to presence of hypofluorite or a fluorate.

Electrolysis of a fused mixture of KOH and KF yielded a product which on acidification with nitric acid gave a precipitate containing silver and fluorine. This was probably a fluorate.

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Herbert Fineberg

HYDROGEN BONDING AND ITS RELATION TO SOLUBILITY

Historical

The concept of the hydrogen bond was first introduced by Werner in 1903 to account for the reaction between NH_3 and HCl in the vapor phase, and the combination of NH_3 and H_2O. Later, Pfeiffer, in 1913, used this concept to explain some anomolies in organic compounds. Latimer and Rodebush in 1920 explained the association of liquids on the basis of hydrogen bonding.

Examples explained by hydrogen bonding include the following: structure of KHF_2, polymerization of HCN, dimerzation of fatty acids in non-polar solvents and in the vapor state, association of alcohols, chelate compounds, deviations from Raoult's law, α and β oxalic acid, etc.

Solubilities explained by hydrogen bonding:

The general types of hydrogen bonds are OH <-- O, OH <- N, OH <--X, NH <--N, CH <--O, and CH <- N. It is possible that hydrogen bonds with other elements but if so the bonds are too weak to be measured. The CH link shows quite a range of bonding strength. In methane no hydrogen bonding can be detected, but if two or three of hydrogen atoms are replaced by electronegative atoms such as Cl or F then the bonding strength becomes appreciable. The presence of the strongly electron-attracting halogen atoms on the carbon loosen the hydrogen and make it available for coordination to the donor atom. Hence, the strength of the bridging should increase in the order F > Cl > Br > I, thus increasing the solubility. This was found to be so.

The solubility of $CHCl_2F$ was determined in a large number of solvents. Generally the solvents contained donor atoms and were of the following types: ethers, thioethers, esters, ether-esters, ketones, aldehydes, alcohol-ethers, amines, amides, nitriles, hydrocarbons, and their halogenated derivatives. The results of these investigations are summarized below.

a) <u>Ethers</u> produce high solubility. Highest solubilities are obtained with polyethylene glycol ethers. One might expect that the solubility would be proportional to the number of ether linkages in the molecule. The solubility does increase with the number of ether linkages, but it has been shown that only alternate oxygen atoms act act donors. Solubility in cyclic ethers suck as dioxan, is less than in straight chain ethers. Aryl-alkyl ethers such as resorcinol diethyl ether show poorer solvent action than do the alkyl ethers, indicating that the attachment of oxygen by one bond to a benzene nucleus decreases the tendency of the oxygen to act as a donor. Diethyl phthalate, in which the oxygen is separated from the benzene ring by an intervening carbon atom, shows high solvent power. Quite low solubility is encountered in the corresponding thioglycol-ethers. At present there is no explanation for this experimental fact. Low solubility in halogenated ethers would be expected due to the fact that negative halogens decrease the tendency of the oxygen to donate electrons to the hydrogen.

b) <u>Esters</u>-Same relative solubilities as in the ethers.

c) <u>Ketones</u>-Same relative solubility as in the ethers

d) Alcohols -Solubilities are extremely low in the alcohols, due to the fact that the alcohols are highly associated liquids. This association takes place by intermolecular hydrogen bonding. There is considerable evidence that the tendency of hydrogen to act as an acceptor increases in the order H--C < H--N < H--O < H--F, consequently, it is not to be expected that the addition of the $CHCl_2F$ would disrupt the O--H--O bonds to form the less stable

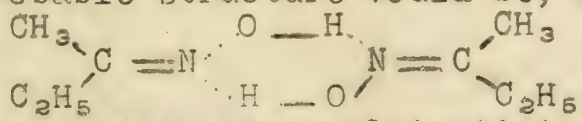
C--H--O Bond.

e) Amines - High solubilites were found in tertiary amines and lower in primary and secondary amines. The lower solubilities are due again to intermolecular association. Here we have striking parallelism between the behavior of alcohols and primary amines, and ethers and tertiary amines.

f) Amides - Extremely low solubility in formamide and acetamide is due again to intermolecular hydrogen bonding. However, the solubility was quite high in N-dimethyl acetamide and other completely substituted amides, showing that lack of intermolecular hydrogen bonding is conducive to high solubility. The extremely low solubility in unsubstituted amides leads to the conclusion that they form polymers rather than dimers, and this has been borne out by other methods of study.

g) Acids-Solubilities are slightly lower than ideal values but are much higher than in alcohols, i.e., acids stop at the dimer stage while alcohols are more highly associated.

h) Oximes-The only oxime in which the solubility was determined was methyl ethyl ketoxime in which the solubility was almost normal. This suggests that oximes form dimers analagous to the fatty acids. The probable structure would be,



Cryoscopic measurements also substantiate this point of view.

i) Nitriles and dinitriles - Solubilities were found to be quite high in nitriles. In dinitriles, however, such as $CN(CH_2)_2CN$, the solubility was quite low. The CN groups activate the methylene group and make the hydrogen labile, causing association to take place. In $CN(CH_2)_3CN$ the cumulative effect is decreased, so there is less association and therefore greater solubility. When the number of methylene groups is increased to four or more this effect is overcome by the distance between the nitrile groups and the solubility increases to a maximum.

j) Unsaturation - The presence of unsaturated bonds in the molecule containing a donor atom showed very little effect.

k) Hydrocarbons - They show practically no deviation from the ideal values, as is to be expected, because there is no opportunity for hydrogen bonding.

Other Solutes.

a) Completely halogenated methane. The solubilities of CCl_2F_2 and CCl_3F were measured in a wide variety of solvents and in practically every case the solubility was lower than that calculated from Raoult's law.

b) Acetylenes. Since the presence of the highly electronegative halogen atoms on the carbon atom of a haloform activates the hydrogen and makes it available for coordination, it is logical to expect that other strongly negative groups attached to a CH radical will lead to the same behavior on the part of the hydrogen. Such groups occur in the acetylenes. The solubility of acetylene and phenyl acetulene are greatly in excess of the calculated values.

c) Solid solutes containing donor atoms. The solubility of many of these solutes were determined in $CHCl_3$, CCl_4, $CHCl\ CCl_2$, $Cl_2C\ CCl_2$, and $CHCl_2CHCl_2$. In general, as would be expected, the solubilities were much greater in hydrogen containing halogenated hydrocarbons than in completely halogenated hydrocarbons.

From all the data it was found that the nitrogen atom of N-disubstituted amides is the best electron donor for forming hydrogen bonds.

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Reported by T. D. O'Brien
March 19, 1940

NITROGEN TETRASULFIDE

Preparation

In the preparation of N_4S_4 the spurce of nitrogen is NH_3 and sour of sulfur is S_2Cl_2, SCl_2, S, $SOCl_2$, and CS_2.

I. Sulfur monochloride

a. Gregory (1) - S_2Cl_2 was dropped into an excess of aqueous ammonia and the mixture was allowed to stand until the solution becomes yellow. The solution is treated with alcohol and the sulphuric crystallized out. This leaves N_4S_4 in the mother liquor.

$$6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 12NH_4Cl + 8S$$

b. Schenck (4) prepared N_4S_4 by passing dry NH_3 into a benzene solution of S_2Cl_2.

c. Valkenburgh and Bailar (5) used ether as solvent for the S_2Cl_2.

d. Macbeth and Graham (6) dissolved S_2Cl_2 in $CHCl_3$

II. Sulfur dichloride

a. Souberain (2) passed NH_3 into SCl_2. The reaction mixture was treated with cold water in order to remove the NH_4Cl formed and the excess SCl_2. This treatment left the N_4S_4 as a residue.

$$6SCl_2 + 16NH_3 \longrightarrow N_4S_4 + 2S + 12NH_4Cl$$

b. Fordos and Gelis (3) employed CS_2 as a solvent, and passed dry ammonia into the solution until a yellow solution results. NH_4Cl formed is separated by filtration. Evaporation of the solvent yielded N_4S_4.

c. Francis and Davis (7) dissolved the SCl_2 in benzene forming a 10-15% solution, and NH_3 was passed into the solution. The NH_4Cl was filtered off and evaporation gave N_4S_4. The product was purified by crystallization from boiling benzene.

d. Vosnessensky (9) used a mixture of NH_3 and air which he passed into a 20% solution of SCl_2 in anhydrous benzene. The reaction mixture is filtered of its NH_4Cl. The solution is evaporated, and the residue is extracted by a soxhlet extractor with benzene. The product is recrystallized from benzene.

III. Sulfur

Ruff and Geisel (11) dissolved sulfur in liquid ammonia which formed N_4S_4 and H_2S

$$10S + 4NH_3 \longrightarrow 6H_2S + N_4S_4$$

The H_2S formed was precipitated as Ag_2S. The N_4S_4 was obtained by evaporation, heating at 100°, and extraction with CS_2

IV. Thionyl Chloride

Michaelis (11) treated thionyl chloride with NH_3, and the N_4S_4 formed was extracted with CS_2 and recrystallized from CS_2.

V. Carbon Disulfide

Ruff and Geisel (11) passed NH_3 into a benzene solution of CS_2

Properties

N_4S_4 is an orange-red crystalline product which melts at 178-80°. It is insoluble in water, but soluble in benzene, CS_2 and liquid ammonia. At 20°, N_4S_4 has a specific gravity of 2.2.

Reactions

I. Amines (4)

a. Primary - Benzylamine was treated with N_4S_4 in ratio the 6:1

$$C_6H_5\text{-}NH_2 + N_4S_4 \longrightarrow Ar\text{-}\underset{\underset{S}{\|}}{C}\text{-}N{=}S + N_2 + NH_3$$

Schenck called the compound formed a thioamide and found it to melt at 104-5°.

b. Secondary

1. Dimethylamine

$3N_4S_4 + 24(CH_3)_2NH \rightarrow 12(CH_3)_2N-S-N(CH_3)_2 + 8NH_3 + 2N_2$

2. Piperidine

$3N_4S_4 + 24C_5H_{10}NH \rightarrow 12C_5H_{10}N-S-N(CH_3)_2 + 8NH_3 + 3N_2$

c. Phenyl hydrazine

$N_4S_4 + 4C_6H_5-NH-NH_2 \rightarrow 4S + 8/3NH_3 + 2/3N_2 + 4C_6H_5\overset{-N-H}{\underset{N}{\|}}$

$4C_6H_5-\overset{-N-H}{\underset{N}{\|}} \rightarrow 4C_6H_6 + 4N_2$

II. Hydrogen fluoride reacts in presence of water to form thionyl fluoride. $6HF + \underset{N}{\|}_4S_4 + 3H_2O \rightarrow 3SOF_2 + 4NH_3 + S$

III. Reduction with stannous chloride and alcohol yielded $(HSN)_4$. The exact mechanism is not known, but the absence of acetaldehyde in the products led to the proposing of the following mechanism. (12)

$2SnCl_2 + 4EtOH \rightarrow 2Sn(OEt)_2 + 4HCl$

$2Sn(OEt)_2 + 4EtOH + S_4N_4 \rightarrow (HSN)_4 + 2Sn(OEt)_4$

a. With formaldehyde and heated in presence of alkali forms $(NSCH_2OH)_4$ (12)

$(HSN)_4 + 4HCHO \rightarrow (NSCH_2OH)_4$

b. $AgNO_3$ (16)

$(HSN)_4$ was dissolved in acetone and treated with a acetonitrile solution of $AgNO_3$ diluted with acetone. A golden precipitate was obtained of $(HSN)_4.2HgNO_3$.

c. Reactions in liquid ammonia (16)

1. Potassium dissolved in liquid NH_3 and treated with $(HSN)_4$ formed the compound $KNH_2.KSN$.

2. Nitrogen tetrasulfide dissolves in liquid ammonia. The addition of PbI_2 to this solution causes an addition salt to be formed.

$2(NS)_4 + 4NH_3 \rightarrow (HSN)_4 + (NH_2-SN)_4$

$+$

$4PbI_2 \rightarrow 4PbN_2S.N_4S_4.3NH_3 + 8NH_4I$

d. Further reduction (16)

1. Continued reduction by $SnCl_2$-EtOH yields NH_4HS. Neuwesen postulated an analogy with HCN. Just as its impossible to find methylene imide as intermediate in the reduction of HCN, likewise it is impossible to find thiohydroxylamine as as an intermediate.

$(HSN)_4 + 4H_2 \rightarrow (H_2S:NH_4)_4 + 4H_2 \rightarrow 4H_3S.NH_2$

$\downarrow$

$4HS.NH_4$

2. Reduction by Na and alcohol yielded Na_2S and NH_3

IV. Formation of thio trithiaz salts $N_3S_4^+$ (13)

a. Chloride is obtained by heating N_4S_4 with S_2Cl_2 or with CH_3COCl The mechanism is not quite understood

b. Bromide is prepared like the chloride

c. Nitrate is obtained from the chloride by a concentrated solution of $NaNO_3$.

d. Iodide is prepared from S_4N_4 by treating it with a cold solution of KI.

e. Thiocyanate is made from chloride by soln. of KCNS.

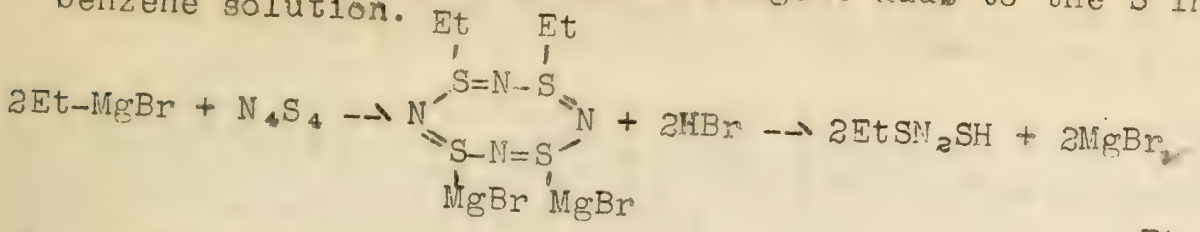
V. Addition Compounds. (14) (15)

a. N_4S_4 forms addition compounds with salts at some amphoteric elements in inert solvents. N_4S_4, $TiCl_4$; $N_4S_4.SbCl_5$, etc. There is no reaction with $FeCl_2$, $AsCl_3$, $SnCl_2$, $SbCl_3$, PCl_3. The best solvent is CCl_4.

b. At low temperatures forms addition compounds with SCl_2 and SBr_2 in CS_2.

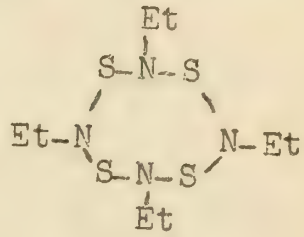
VI. Grignard Reagent. (16)

Meuwesen found that grignard reagent adds to the S in N_4S_4 in benzene solution.



Reaction seems to be analogous to:

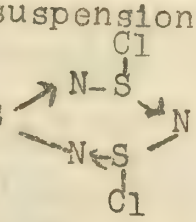
$$4SCl_2 + 12Et\text{-}NH_2 \rightarrow (EtNS)_4 + 8EtNH_2.HCl$$



VII. Halogens (13)(17)

a. When chlorine passed through a suspension of N_4S_4 in $CHCl_3$, $(NSCl)_3$ is formed.

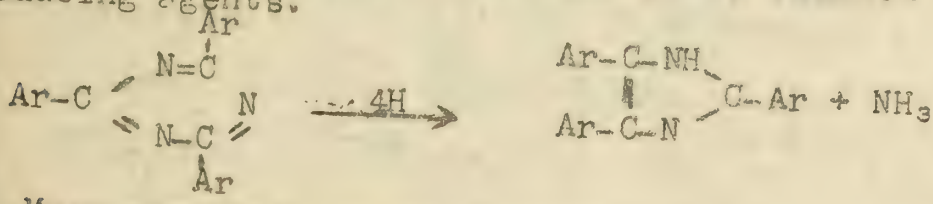
$$3N_4S_4 + 6Cl_2 \rightarrow 4(NSCl)_3$$



b. Bromine reacts the same way. These compounds are soluble in benzene, chloroform, carbon tetrachloride, and carbon disulfide.

VIII. Aromatic aldehydes (18) react vigorously at boiling point with N_4S_4.

$N_4S_4 + Ar\text{-}CHO \rightarrow (NCAr)_3 + SO_2 + H_2O$. The exact mechanism is not known, but also a little lophin was found ($C_3N_2HAr_3$). Compound is stable to KOH solutions, and it is reduced to lophin by mild reducing agents.



More powerful reducing agents yield Ar-COOH and NH_3.

Structure

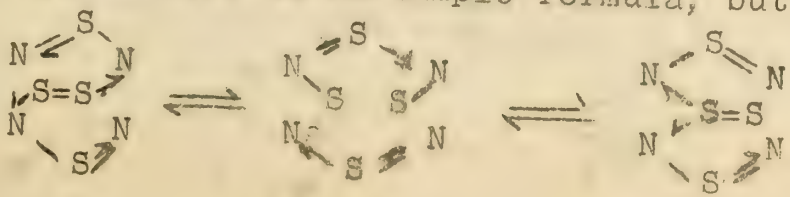
Valkenburgh and Bailar found that hydrolysis of N_4S_4 gave NH_3, $S_5O_6^{=}$, $SO_3^{=}$ and S, but offered no mechanism to explain structure.(5) Meuwesen postulated the following reaction: (12)

$$N_4S_4 + 6NaOH + 3H_2O \rightarrow Na_2S_2O_3 + 2Na_2SO_3 + 4NH_3$$

he also added that if any hyposulfite formed would decompose as follows:

$$2Na_2S_2O_4 + H_2O \rightarrow Na_2S_2O_3 + 2NaHSO_3$$

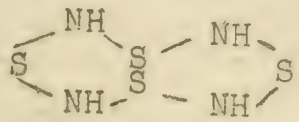
Arnold, Hugill, and Hutson (10) claimed that no adequate structure had been proposed up to this time (1936). They added that the compound is not a nitrogen sulfide but a sulfo nitride because hydrolysis gives NH_3 and H_2S. There is no simple formula, but exists in resonating forms.



a. b. c.

Evidence for above structures:

1. Hydrolyzee quantitatively by cold dilute alkali
2. Reduction gave no hydrazine. Consequently no two nitrogens connected
3. Chlorine reacts to form $(NSCl)_3$
4. Forms addition compounds with amphoteric metal salts
5. Reduced by $SnCl_2$-EtOH to $(HSN)_4$ which shows a puckered octagonal ring like rhombic sulfur.



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R. Steinman

ACID BASE REACTIONS IN NON-PROTONIC SOLVENTS

A. Introduction

1. The growth of our ideas of acid-base phenomena has been mainly one of expansion to include increasing numbers of solvent systems.
2. At first these were limited to the water system by definition.
3. Brönsted broadened our concept to include any solvent having an exchangeable proton.
4. It no longer seems sufficient to limit ourselves to protonic solvents by the retention of the hydrogen ion or proton as an essential property of an acid.

B. Extent of concept

1. Properties and reactions indicative of acid-base reaction
   a. Electrolytic solutions
   b. Well defined acids, bases, and salts
   c. Neutralization reactions giving rise to salts and showing definite poteniometric endpoints.
   d. Formation of solvates
2. Liquid SO_2 (Jander)
   a. Solvent itself is slightly ionized

$$3SO_2 \rightleftharpoons (SO.SO_2)^{++} + SO_3^{--}$$

   b. Acids $SOCl_2$, $SOBr_2$, $SOAc_2$, $SO(SCN)_2$
      Bases Cs_2SO_3, Na_2SO_3
      Salts CsCl, NaCl
   c. Reaction gives typical neutralization curve

$$SOCl_2 + Cs_2SO_3 \rightleftharpoons 2CsCl + 2SO_2$$

   d. Ammonia or organic amines gives solvation followed by solvolysis (Strictly analogous to reaction between NH_3 and water)

$$(1)\ 2NH_3 + 2SO_2 \rightleftharpoons \begin{pmatrix} NH_3 \\ NH_3 \end{pmatrix} SO^{++} + SO_3^{--}$$

$$(2)\ NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

      In (1) the SO_3^{--} formed may be neutralized by a solution of $SOCl_2$
   e. Amphoterism

$$2AlCl_3 + 3[(CH_3)_4N]_2SO_3 \rightleftharpoons Al_2(SO_3)_3 + 6(CH_3)_4NCl$$

$$Al_2(SO_3)_3 + 3[(CH_3)_4N]_2SO_3 \rightleftharpoons 2[(CH_3)_4N]_3Al(SO_3)_3$$

$$3SOCl_2 + 2[(CH_3)_4N]_3Al(SO_3)_3 \rightleftharpoons Al_2(SO_3)_3 + 6(CH_3)NCl + 6SO_2$$

3. Liquid phosgene (Germann)
   a. Electrolysis

$$COCl_2 \xrightarrow{E} \underset{\text{cathode}}{CO} + \underset{\text{anode}}{Cl_2}$$

   b. Acid $COAl_2Cl_8$
      Base NaCl
      Salt $NaAlCl_4$

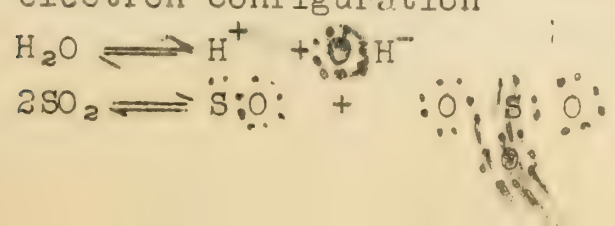
c. Neutralization

$$COAl_2Cl_8 + 2NaCl \longrightarrow 2NaAlCl_4 + COCl_2$$

d. Solvation - addition compounds of phosgene with $AlCl_3$, $TiCl_4$, $SnCl_4$.

4. Acid-Base phenomena in some organic solvents
   a. Common acids in benzene or other non-polar solvents could be titrated by solutions of sodium ethoxide in ethyl alcohol (Flanders)
   b. Platnikov has developed a method for electroplating aluminum from a solution of aluminum bromide in ethyl bromide.

C. Theories and Concepts which have to date been advanced to generalize the definitions of acids.
   1. Germann
      a. A True Acid is a solute which on solution gives rise to the cation characteristic of the solvent and to an anion which contains the anion of the solvent.
      b. A True Base is a solute which upon solution gives rise to the anion of the solvent and simple metal cations.
      c. Objections to Germann's definitions
         (1) Solutions such as HCl in H_2O or $SOCl_2$ in SO_2 are not treated as acids.
         (2) Places restriction based upon the solvation of the anion of the acid.
      d. Advantage - leads to explanation of the acidity of metal ions in a solution similar to that used by Bronsted for protonic solvents.
   2. Cady and Elsey
      a. an acid is a solute which gives rise to a cation characteristic of the solvent.
      b. a base is a solute which gives rise to an anion characteristic of the solvent
      c. Limitation - solvent must be only slightly ionized in order that there will be a driving force for neutralization reactions.
   3. Lewis - no regard to solvent.
      a. an acid is a substance containing an atom which may accept a free pair of electrons from another atom
      b. a base is a substance which has a free pair of electrons available to complete the configuration of another atom.
   4. Smith - modification of Lewis' approach.
      a. An acid is a solute whose molecule, neutral or charged, which accepts a pair of electrons from the molecule or anion of the solvent.
      b. a base acts as the donor of a pair of electrons to an ion or a molecule of the solvent.
      c. Advantage - leads to same results as Bronsted concept, but also applies to non-protonic solvents.
   5. Wickert - necessity of a "water-like" solvent.
      a. The term "water-like" solvents is applied to a substance which ionizes to give a cation having an incomplete electron configuration



(1) An acid is a substance which on solution gives rise to a cation having incomplete electron configuration and to anions having a complete electron configuration

(2) A base and a salt are substances which on solution give rise to both cations and anions having complete electron configuration. The base has an anion common with the solvent.

b. Limitations

(1) Restricted to slightly ionized solvents since from energy considerations such an ionization could not proceed to any marked degree.

(2) Omits such solvents as molten NaCl and molten NaOH, since on ionization these give cations having a complete electron configuration.

$$NaCl \rightleftharpoons :\ddot{\underset{\cdot\cdot}{Na}}:^{+} + :\ddot{\underset{\cdot\cdot}{Cl}}:^{-}$$

$$NaOH \rightleftharpoons :\ddot{\underset{\cdot\cdot}{Na}}:^{+} + :\ddot{\underset{\cdot\cdot}{O}}:H^{-}$$

3. Conclusions

(1) Any acid which gives rise to the same ions in the pure state that it does in solution, must itself be a "water-like" solvent in the pure state.

(2) Any substance which is an acid in one "water-like" solvent is an acid in any other "water-like" solvent in which it undergoes a similar ionization.

(3) A substance which is a base or a salt can never become an acid or a "water-like" solvent unless its manner of ionization varies with conditions.

(4) There are only two types of ionic compounds: those which ionize as acids or solvents, and those which ionize as bases or salts.

(5) There is no essential difference between the processes of neutralization, displacement, and solvolysis

$$NaOH + HCl \rightleftharpoons NaCl + H_2O$$

$$BaCl_2 + H_2SO_4 \rightleftharpoons BaSO_4 + 2HCl$$

$$NaC_2H_3O_2 + H_2O \rightleftharpoons HC_2H_3O_2 + NaOH$$

Reference:

J. Chem. Education, 17, 116-9 (1940) March
A bibliography of eighteen articles is given on page 119.

The Binary System $ZnCl_2$ - NH_4Cl

I. This system is of real importance because of the use of a $ZnCl_2$, NH_4Cl complex as a fluxing agent for the hot-galvanizing process

II. K. Hachmeister (1919) made a thorough study of the system. His temperature-concentration diagram shows:

(a) melting point of $ZnCl_2$ 283° C; boiling point 732° C.
(b) a stable complex, $3ZnCl_2.NH_4Cl$, formed at 33 and % NH_4Cl; melting point 249° C; dissociation temperature 350° C.
(c) an eutectic between $ZnCl_2$ and $3ZnCl_2.NH_4Cl$ at a point 27 mol % NH_4Cl and a temperature of 232° C.
(d) a second eutectic at 48 mol % NH_4Cl, temperature of 180° C.
(e) the melting point of the mixture becomes greater than the dissociation temperature at a point approximately 60 mol % NH_4Cl and a temperature of 342° C.
(f) the transition temperature for the change α- to β- NH_4Cl at 174° C. (A more accurate value was recently determined. It is 184.5° C)
(g) the sublimation or dissociation temperature of NH_4Cl is 338°C.
(h) the formation of three known complexes of $ZnCl_2.NH_4Cl$ having the ratios of 1:2, 1:3, and 1:4 could not be shown by the diagram.
(i) complex double-salts form when an intimate mixture of correct proportions of the dry, unfused salts are heated.

III. To explain the dissociation of the $ZnCl_2.NH_4Cl$ complexes, two related systems must be examined.

(a) The NH_4Cl - NH_3 system

$NH_4Cl.6NH_3$) dissociation temperature below 0° C
$NH_4Cl.3NH_3$)

(b) The $ZnCl_2$ - NH_3 system

$ZnCl_2.10NH_3$	dissociation	temperature -	about 0° C
$ZnCl_2.6NH_3$	"	"	57.5°
$ZnCl_2.4NH_3$	"	"	149°
$ZnCl_2.2NH_3$	"	"	271°

$ZnCl_2.NH_3$ can be distilled at red heat without decomposition

This last compound is probably the only complex which exists above 342° C. $ZnCl_2.xNH_4Cl$ must dissociate as follows:

$$ZnCl_2.xNH_4Cl \xrightarrow{\Delta} ZnCl_2(x-1)NH_4Cl.NH_3 + HCl$$
$$\downarrow$$
$$ZnCl_2(x-1)NH_4Cl + NH_3$$

This process is repeated progressively with only $ZnCl_2.NH_3$ remains.

IV. The ammonium chloride flux used in galvanizing is a mixture of zinc ammonium salts. The reactions for the formation of a new flux is as follows:

$$Zn + 2NH_4Cl \rightarrow Zn(NH_3)_2Cl_2 + H_2$$
$$Zn(NH_3)_2Cl_2 \rightarrow Zn(NH_3)Cl_2 + NH_3$$

When old flux is reinvigorated by the addition of NH_4Cl, the reaction is probably:

$$ZnO + 2NH_4Cl \rightarrow ZnCl_2.NH_3 + NH_3 + H_2O\uparrow$$

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H. F. Jones

Inorganic Seminar April [illegible] 1941

FLUOROSULFONIC ACID AND SULFURYL FLUORIDE

A. Introduction

Fluorosulfonic acid and sulfuryl fluoride may both be considered derivatives of sulfuric acid. When only one of the hydroxyl groups in sulfuric acid is replaced by halogen the acid properties are still retained, but the acidic characteristics disappear when both hydroxyl groups are replaced.

The stability of these substituted sulfuric acids decreases as heavier halogen atoms are substitued, fluorosulfonic acid being most stable. It is only partially decomposed by water according to the following equation: $HSO_3F + H_2O = H_2SO_4 + HF$
When water is added in equimolar quantities to the acid, less than 1.4% of sulfuric is formed.

Likewise as in the above series the disubstituted compounds decrease in stability as heavier halogens are substituted in sulfuric acid. Sulfuryl fluoride is not decomposed by water even at 150°. However sulfuryl chloride is acted on by water in the cold if allowed to stand for some time.

B. Preparations

1. Fluorosulfonic Acid

a) Fluorosulfonic acid may be prepared from hydrofluoric and sulfuric acids, and is present in large quantities in a mixture of them as prepared from calcium fluoride and sulfuric acid. It can be obtained by distilling this mixture. A mixture of HF and KF plus fuming sulfuric acid has been used with yields of 85%

b) Fluorosulfonic acid is formed when hydrogen fluoride and sulfur trioxide are brought together: $SO_3 + HF \rightarrow HSO_3F$.

c) The potassium salt of fluorosulfonic acid is obtained from potassium pyrosulfate, which contains labile sulfur trioxide, when heated with potassium fluoride:

$$K_2S_2O_7 + KF \rightarrow KSO_3F + K_2SO_4$$

d) A modification of the method in (a) was used by Trautz and Ehrmann. They heated a mixture of 60% oleum and calcium fluoride, distilled off the acid produced. Yields of 60-65 g. were obtained from 200 g. of oleum.

The acid is now being produced in Great Britain by the method shown in (b). Equimolar proportions of sulfur trioxide and hydrogen fluoride are passed continuously through a reaction tube made of aluminum. One or both of the reactants may be in the liquid state.

2. Sulfuryl Fluoride

a) Sulfuryl fluoride may be prepared from sulfur dioxide and fluorine. The reaction is only completed after it has been induced by means of a glowing platinum wire.

b) Sulfuryl fluoride is formed very readily by heating dry barium fluorosulfonate: $Ba(SO_3F)_2 \rightarrow BaSO_4 + SO_2F_2$ (60% yield)
The barium fluorosulfonate may be prepared from fluorosulfonic acid and barium fluoride: $HSO_3F + BaF_2 \rightarrow Ba(SO_3F)_2$

c) The gas may also be prepared from fluorine and damp hydrogen sulfide.

C. Properties and Reactions:

1. Fluorosulfonic Acid

a) Physical Properties: It is a mobile, colorless liquid, fumes in air, b.p. 162.6°, on distillation it undergoes slight

decomposition into sulfuryl fluoride and sulfuric acid. It is soluble in nitrobenzene without decomposition. Its alkali salts are fairly stable to heat. The known salts of this acid are all easily soluble in water, even the silver, copper, barium and lead salts.

b) Reactions. 1) A series of aromatic fluorosulfonates have been prepared by Lange and Müller in yields ranging from 5 to 43% by heating the corresponding diazonium fluorosulfonic acids, e.g., phenyl, o-tolyl, p-chlorophenyl, p-nitrophenyl. All these products were stable to water and acids but slowly hydrolyze in alkali. These aromatic fluorosulfonates are useful for combating moths, etc.

2) Meyer and Schramm showed that fluorosulfonic acid in the cold does not attack sulfur, carbon, selenium, tellurium, lead, silver, copper, zinc, iron, chromium or manganese but slowly dissolves mercury and tin. At higher temperatures it dissolves sulfur, lead, mercury and tin rapidly. Rubber, cork, wood, and sealing wax are instantly decomposed by the acid. Carbon tetrachloride does not react or mix with it; acetone is immediately reacted upon and gives a dark red color which can be used as a means of detecting the acid. Benzene reacts with HSO_3F to give $PhSO_3H$, ether or absolute alcohol gives ethyl fluorosulfonate. Methyl fluorosulfonate prepared analogously boils at 92°, corrods glass, and reacts with phenol to give anisol. Ethyl fluorosulfonate boils at 113° and has a density of 1.310 at 25° C.

2. Sulfuryl Fluoride - This compound is an odorless very inert gas. m. p. - 121.4 ± 0.5°, b.p. -49.7± 0.3° at 748.5 mm. and -49.4° at 760 mm. Vapor pressure, 10 mm. at - 196°, 22 mm. at - 150°, 246 mm. at -78°. Density at 16.6° and 754.6 mm. is 3.49 (calc. 3.52)

Solubility and hydrolysis of SO_2F_2 is shown in the following table.

100 cc. of SO_2F_2 (at 19.5°C) added to KOH as follows:

reacts with 25 cc. of	5% KOH	- 28 cc. in 1.5 hrs.
	5% KOH	- 26 cc. in 1 hr.
	10% KOH	- 54 cc. in 3/4 hr.
	25% KOH	- all in 20-25 min.
	50% KOH	- all in 15 min.

Alcoholic KOH reacts rapidly with SO_2F_2

10 cc. H_2O	dissolves	0.5 cc.	SO_2F_2	(0.4%)
10 cc. alcohol	"	3.4 cc.	"	(3.7%)
10 cc. toluene	"	22 cc.	"	(21%)
10 cc. CCl_4	"	13.8 cc.	"	(13.6%)

10 cc. $KMnO_4$ solution shows no chemical reaction.
10 cc. conc. H_2SO_4 no reaction.

Thermal decomposition of SO_2F_2. - SO_2F_2 when passed through a glass tube at 400° remains unchanged. At 420-440° it decomposes into SO_2 and SO_3, and SiF_4 (from glass). No SF_6 was found as had been previously reported.

The reaction:

$$3SO_2F_2 \rightarrow 3SO_3 + SF_6$$ could not be demonstrated as occurring.

It is of interest to note that sulfuryl chlorofluoride has just recently been prepared by Booth and Herrman by the action of SbF_3 and SO_2Cl_2 in the presence of $SbCl_5$ under pressure. It is hydrolyzed by water and absorbed by NaOH. No reaction at room temper-

ature with glass, mercury or brass was observed.
The structure of sulfuryl fluoride has been investigated by Stevenson and Russell, by the electron diffraction technique. The interatomic distances and bond angles are: S-F = 1.56 ± 0.02 Å, S-O = 1.43 ± 0.02Å, LF-S-O = 105 ±2°, and LF-S-F = 100 ± 10°.

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Reported by T. W. Mastin
April 9, 1940

INORGANIC SEMINAR

April 23, 1940

TECHNICAL ADVANCES IN INORGANIC CHEMISTRY DURING THE PAST TWENTY-FIVE YEARS.

1. The Actual and Potential Raw Materials of the Inorganic Chemical Industry - Mr. Keller
2. The Commoner Metals - Mr. Brasted
3. The Rare Metals - Mr. Brimm
4. Electrodeposition and Electro-refining of Metals - Mr. McClellan
5. The Halogens - Mr. Bernays
6. Sulfur - Mr. Speck
7. Phosphorus - Mr. Toy
8. The Alkali Industry - Mr. Work
9. Nitrogen - Mr. Steinman
10. Silicon and Silicates - Mr. O'Brien

Inorganic Seminar - CHEMISTRY OF CYANAMIDE

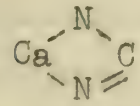
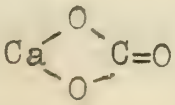
I. Introduction

The discovery of calcium cyanamide is credited to Frank and Caro for their work in 1897 in which they were attempting to synthesize a cheap cyanide for gold and silver extraction. It was an early source of fixed nitrogen, but due to conversion costs it has given way to the synthetic ammonia process. At the time of the World War, the price was prohibitive, but since then the price of the dimer, dicyanamide, has been reduced to a price so it is now sold in carload lots. It is used in the synthesis of barbiturates and thiourea for the making of resins. Cyanamides are of industrial and also scientific importance because of their resemblance to other compounds in their reactions.

II. Cyanamide is an ammonocarbonic acid

A. Franklin points out (1) that cyanamide is the analog in the ammonia series of CO_2 and (2) that $CaCN_2$ and $CaCO_3$ are analogous

(1) O=C=O NH=C=NH

(2)  

B. $CaCN_2$ is hydrolyzed commercially to form NH_3 and $CaCO_3$ by autoclaving with H_2O.

$$CaCN_2 + 3H_2O \rightleftharpoons CaCO_3 + 2NH_3$$

The reverse of this reaction takes place with finely divided $CaCO_3$ subjected to a current of ammonia heated to 700-800°C.

III. Reduction of $CaCN_2$

A. The reduction of $CaCN_2$ by carbon is analogous to the reduction of CO_2

$$CaCN_2 + C \rightleftharpoons Ca(CN)_2$$

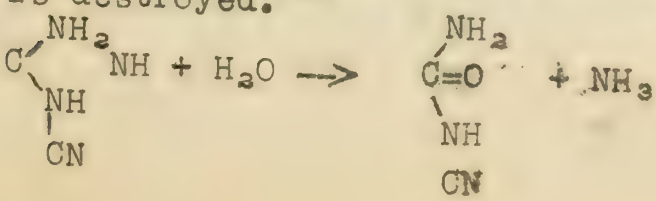
$$CO_2 + C \rightleftharpoons 2CO$$

B. $Ca(CN)_2$ is prepared by the fusion of $CaCN_2$ [illegible] with free carbon and salt in an electric furance. To prevent reversion the $Ca(CN)_2$ must be cooled quickly. This is done by a water-cooled flaking wheel. The final product consists of 47% $Ca(CN)_2$

IV. Polymeriztion of cyanamide

A. Steps

1. Hydrolysis of $CaCN_2$
   $2CaCN_2 + 2H_2O \longrightarrow Ca(HCN_2)_2 + Ca(OH)_2$
2. Precipitation of the Ca^{++} by H_2SO_4 with p.H. of 5
3. Dicyanamide is formed by action of a cyanamide ion and an undissociated molecule
   $(NHCN)^- + H_2NCN \longrightarrow (NHC{=}NHHNCN)^-$
4. The velocity of formation of dicyanamide is at maximum at p.H 9.6. Above p.H. 10 cyanurea is formed and dicyanamide is destroyed.



5. The above reaction explains why $CaCN_2$ can be used on soils only in limited amounts. When $CaCN_2$ are added above buffer capacity, dicyanamide is formed and produces toxicity in plants.

V. Hydrolysis of cyanamide

A. The hydrolysis of cyanamide to urea in alkaline solutions is a reaction of first order.

$$HN_2CN + H_2O \rightarrow NH_2CONH_2$$

B. If p.H. is above 4 in acid solution very little $CO(NH_2)_2$ is formed. In acid solutions below p.H. 4 the velocity of hydrolysis is proportional to acid concentration.

$$H_2NCN + H^+ \rightarrow H_3NCN^+$$

$$H_3NCN^+ + H_2O \rightarrow H_3NCO.NH_2^+ \rightarrow H_2NCONH_2 + H^+$$

VI. Reaction of cyanide and cyanamide

A. $Ca(COOH)_2$ and $Ca(C_2H_2O_4)_2$ are formed when crude $Ca(CN)_2$ is autoclaved. This is due to the presence of $CaCN_2$.

VII. Reaction of cyanamide and hydrogen sulfide

A. Under controlled p.H. conditions, HS^- passed through cyanamide gives thiourea

VIII. Reaction of cyamide and ammonia

A. After an ammonium salt is formed, a rearrangement into guanidine occurs.

$$HN=C=NH + NH_3 \rightarrow HN=C=N-NH_4 \rightarrow NH=C\begin{matrix}NH_2\\NH_2\end{matrix}$$

IX. Analogous reactions

A. The reactions of cyanamide in aqueous solutions is analogous to the carbonyl groups in ammonia reactions.

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Oct. 1940

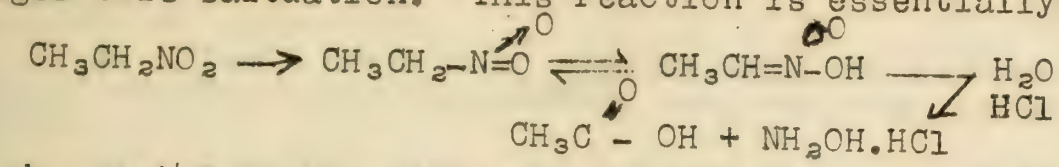
Edward Lemon

INORGANIC SEMINAR October 29, 1940

HYDROXYLAMINE

I. Introduction.

Hydroxylamine has been known for a number of years as an extremely reactive and useful compound, but heretofore has been available only at a high price and for this reason its commerical applications have been extremely limited. The manufacture of hydroxylammonium salts through the acid hydrolysis of a primary nitroparaffin changes this saituation. This reaction is essentially:



The cheapest form in which hydroxylamine is now available is a crude acid sulfate.

II. The preparation of hydroxylamine salts.

1. Reduction of nitric oxide, nitric acid, nitrous acid and certain nitrates by nascent hydrogen.
2. Reduction of nitrous acid and nitrates such as ammonium nitrate, sodium nitrate and potassium nitrate by tin and hot concentrated hydrochloric acid.
3. Reduction of nitric acid by hydrogen in the presence of spongy platinum at temperatures between 115° and 120°.
4. Electrolytic reduction of nitric acid in the presence of hydrochloric acid in a partitioned cell. Cathode portion treated with gaseous hydrogen chloride after electrolysis, precipitating the base as the salt, hydroxylamine hydrochloride.
5. Hydrolysis of aliphatic nitro compounds (supra). Nitromethane, nitroethane, dinitropropane and dinitrobutane have been used.

III. Isolation of hydroxylamine.

1. Loessen attempted to do so by using barium ion to precipitate the combined sulfuric acid as barium sulfate or by using an alcoholic solution of potassium hydroxide, potassium sulfate thereby being precipitated. The aqueous solution was then distilled, but a great part of the hydroxylamine decomposed into ammonia.
2. Bruyn assumed that presence of water was the hindering factor, therefore dissolved the hydroxylamine in methyl alcohol and added sodium methoxide. Sodium chloride filtered off, alcohol removed by distillation.
3. Bruyn also obtained the base by passing ammonia through an ether solution of the complex salt, zinc hydroxylamine chloride. Ether distilled off, and base purified by crystallization from alcohol.
4. Bandisch added finely powdered and dried hydroxylamine sulfate to liquid ammonia in a quartz tube and removed the ammonia by evaporation. Free hydroxylamine extracted with alcohol.

IV. Physical properrtios

1. Anhydrous crystals are without taste or color.
2. Crystals are rhombic and have a sp. gr. of 1.35 at 18°.
3. Melting point is 33°, the sp. gr. of the liquid being 1.2044
4. B. p. is 56-57°/22 mm. At ordinary pressures hydroxylamine decomposes gradually at 15° and at higher temperatures decomposes explosively.
5. Slightly ionized in aqueous solutions as shown by conductivity measurements and molecular depressions of the f. p. of 1.77°, 1.90° and 2.25° respectively for solutions with a mole of hydroxylamine in 1, 30 and 500 liters of solution.

6. Heat of solution equals 3.8 cals/mol.
7. Heat of formation in aq. soln. equals 23.8 cals.
8. Index of refraction equals 1.44047
9. Molecular refraction equals 7.257 and the dispersion equals 0.211
10. Sp. conductivity at a temp. slightly above 33° was approximately 83 times 10^{-6}.

V. Chemical properties.

1. Vapors produce no ill effects, but intravenous injections have poisonous action and nitrous acid can then be detected in the blood.

2. If purity high, can be kept for months without decomposition Decomposition favored by alkalies and a number of salts. Decomposes according to the equations:

$$3NH_2OH \rightarrow N_2 + NH_3 + 3H_2O$$
$$4NH_2OH \rightarrow N_2O + 2NH_3 + 3H_2O$$

Bases favor latter reaction and acids the former.

3. Nitrous acid produced by the alkaline or acid fusion of hydroxylamine. It is supposed that the following reactions take place:

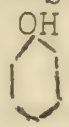
$$2NH_2OH \rightarrow \begin{matrix} HN - NH \\ OH \quad H \end{matrix} + H_2O$$

$$NH_2(OH + H)\begin{matrix} N - NH \\ OH \quad H \end{matrix} \rightarrow (NH_2)_2N\text{-}OH + H_2O$$

$$(NH_2)_2NOH + HOH \rightarrow 2NH_3 + HONO$$
$$HONO + NH_2OH \rightarrow N_2O + 2H_2O$$

4. Some reactions:

a) $NH_2OH.H_2SO_4 + H_2O_2 \xrightarrow{400°} H_2SO_4 + H_2O + HNO_3$

b) 

$+2NH_2OH + H_2O_2 \xrightarrow{aq.}$ 

$+ NH_3 + 3H_2O$

c) $Cl_2, Br_2I_2 + 2NH_2OH \rightarrow 2H(Cl, Br, I) + N_2 + 2H_2O$

d) $HOCl + NH_2OH \rightarrow NH_2OCl + H_2O$
$2NH_2OCl \rightarrow N_2 + Cl_2 + 2H_2O$

e) $2Na + 2NH_2OH \rightarrow 2NH_2ONa + H_2$

f) $Ca + 2NH_2OH \xrightarrow{50°} (NH_2O)_2Ca + H_2$
$(NH_2O)_2Ca + 2H_2O \rightarrow Ca(OH)_2 + 2NH_2OH$

g) $NH_2OH.HCl + NaOH \rightarrow NH_2OH + NaCl + H_2O$

$3NH_2OH \xrightarrow[base]{excess} NH_3 + N_2 + 3H_2O$

h) $NH_2OH + SO_2 \rightarrow NH_2SO_3H$

5. Ox. or red. action depends on conditions:

a. Weakly acid solution:
$4FeCl_3 + 2NH_2OH \rightarrow 4FeCl_2 + N_2O + H_2O + 4HCl$

b. Strongly acid solution--sulfuric acid:
$2FeSO_4 + 2NH_2OH.H_2SO_4 \rightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4 + H_2O$

c. Acetic acid solution, hydroxylamine ox. by iodine, but in conc. hydrochloric hydroxylamine ox. iodine. Mech. of first reaction:

$$2NH_2OH + I_2 \rightarrow 2HI + \begin{matrix} H\text{-}N\text{-}OH \\ H\text{-}N\text{-}OH \end{matrix} \rightarrow \begin{matrix} N\text{-}OH \\ \| \\ N\text{-}OH \end{matrix} \rightarrow N_2O + N_2O$$

d. Iodates, periodates red. by hydroxylamine sulfate:
$2(NH_2OH)_2.H_2SO_4 + KIO_3 \rightarrow N_2O + N_2 + 6H_2O + KI + 2H_2SO_4$
e. CuO and SeO_2 red. by aq. hydroxylamine.

6. Dissolves many salts, as KI, KCN, $NaNO_3$. Solutions of $BaNO_3$ and K_2SO_4 do not give ppt. $BaSO_4$ when mixed.
7. Can unit with many salts as hydroxylamine of crystllization. Is amphoteric, behaving toward alkalis like a weak acid, forming hydroxylamites and towards bases like ammonia, forming salts.

VI. Structure of hydroxylamine.

VII. Derivatives and compounds of hydroxylamine:
1. Red. of cyclic compounds using zinc in an alkaline solution. Heating this hydroxylamine derivative causes shift of OH group to the ring.
2. Synthesis of tetrammines with four different neutral molecules of the $(PtA_1A_2A_3A_4)X_2$ type. Compounds containing three different amines, hydroxylamine, ammonia and pyridine were desired.
3. Hydroxylamine compounds of palladium. Instability of these compound as compared to those of platinum, except in the case of the Magnus salt type $(Pd4A)(PtX_4)$.

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John Whitson

THE INTERCHANGE OF HEAVY OXYGEN BETWEEN WATER AND INORGANIC OXY-ANIONS.

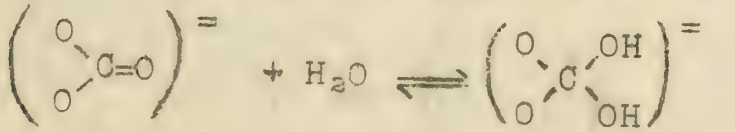
I - Methods of separation of isotopes (1)
- A- Fractional distillation. (2)
- B- Electrolysis.
- C- Hertz diffusion methods
  - 1- Through porous tube
  - 2- Through streaming mercury vapor. (3), (4)
- D- Urey counter-current exchange method
- E- Clusius method
- F- Ultracentrifuge

II- Techniques in exchange investigation
- A- Using oxygen with increased O^{18} concentration
  - 1- Oxy-anion salt dissolved in heavy-oxygen water, let stand for varying lengths of time at several temperatures, water distilled off, and decrease in O^{18} content noted.
  - 2- Heavy oxygen salt used with ordinary water and increase in O^{18} content of water observed.
- B- Using oxygen with decreased O^{18} concentration; methods similar to those above.
- C- Determination of extent of exchange
  - 1- By changes in density of water
    - a- Using pycnometer
    - b- Using quartz or pyrex float. (5)
    - c- Using falling drop method. (6)
  - 2- By refractive index. (1)
  - 3- By mass spectrograph. (1)

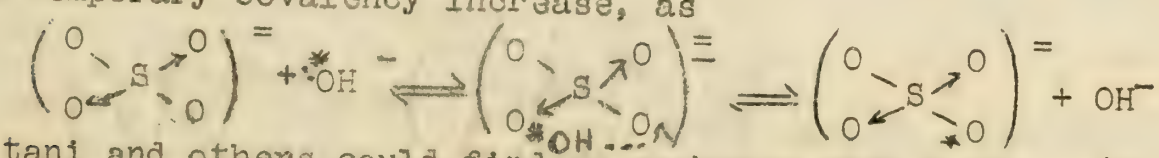
III. Summary of reactions and conclusions
- A- Blumenthal and Herbert found that K_3PO_4 exchanged oxygen atoms with water (7)
  - 1- Postulated that a proton coordinated to one O atom of the PO_4^{---} ion, thus weakening the bond of that O atom to the P atom; an OH^- ion from the ater then replaced the OH group.
- B- Datta and co-workers showed that K_2SO_4 exchanged (8)
  - 1- Reaction catalyzed by hydroxyl ions
  - 2- Suggested three mechanisms for general exchange reactions
    - a- Dehydration followed by hydration, as

$$2PO_4^{---} + 2H^+ \rightleftharpoons 2HPO_4^{--} \rightleftharpoons P_2O_7^{----} + H_2O$$

    - b- Hydration followed by dehydration as



    - c- Temporary covalency increase, as



- C- Titani and others could find no exchange with K_2CO_3. (9)
- D- Titani and Goto studied solutions of K_2SO_4, KNO_3, $NaClO_3$, K_2CO_3, KH_2AsO_4, and KH_2PO_4 (10), (11)
  - 1- No exchange in neutral solution
  - 2- Definite exchange in acidic and basic solutions.

III- E- Mills and Urey used the rate of oxygen exchange to study the velocity of the reaction between CO_2 and H_2O; they concluded that: (12), (13)

1- Exchange of oxygen between CO_2 and H_2O is due to reversible hydration only.

2- Exchange of $NaHCO_3$ occurs only trhough reversible formation of CO_2 by simple hydration

3- K_2CO_3 exchanges slowly, presumably due to reversible reaction of small amounts of CO_2 with hydroxyl ions.

F- Winter and co-workers introduced a variation in technique that resulted in reversal of many findings of others (5)

1- Used silver reaction tubes after showing that oxygen exchange with silicates in glass tubes gave errors.

2- With $NaClO_4$, Na_2SO_4, and K_3PO_4 no measureable interchange occurred in neutral, acid, or alkaline solution.

3- With Na_2SiO_3, H_3BO_3, $Na_2B_4O_7$, $K_2Cr_2O_7$, and acid solutions of $KClO_3$ and KNO_3 definite exchange was found.

4- Concluded that oxygen interchange with oxy-anions occurs only where these are known to react with water, as in the case of silicates, borates, and chromates, or where they are otherwise chemically changed, as in the case of acid solutions of $KClO_3$ and KNO_3.

B- Mills used a pyrex glass container for which he showed that no exchange occurred (14)

1- Results

a- Partial exchange with K_2SO_4 at various acidities, in agreement with mechanism of anhydride formation.

b- Partial interchange with K_2CrO_4 which was greatly retarded by alkali; the mechanism is probably:

$$CrO_3 + H_2O \rightleftharpoons H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \rightleftharpoons 2H^+ + CrO_4^=$$

c- No exchange for K_2SO_3, (?)

d- Definite exchange with $K_2S_2O_3$ and $KMnO_4$

2- Concluded that in general, salts of weak acids exchange due to hydrolysis; salts of strong acids do not exchange unless the solution is acid enough to shift the equilibrium toward anhydride formation.

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J. B. Work

Inorganic Seminar POWDER METALLURGY November 12,1940

I. Introduction

Powder metallurgy is over a hundred years old, and the first metal produced was Platinum which melts at 1755°C. Platinum powder was obtained pure by chemical precipitation and reduction. It was found that by heating to a temperature several hundred degrees below the melting point and then forging the powders seemed to adhere. By repeated heating and forging, ductile Pt was obtained.

The first four developments in the field of powder metallurgy that awoke the industry to the value and use of this process were: (7)

1. Production of ductile, refractory metals. W(m.p. 3370°C), Ta(2850°C), Cb(2500°C) and Mo (2620°C)
2. Production of porous metal bearings.
3. Manufacturing of powder metal contacts and electrode materials.
4. Preparation of hard cemented carbides.

The industry has found that powder metallurgy must be used when certain conditions prevail, as: - (21)

1. When the metal is too refractory to be melted conveniently.
2. When product is required to retain, in proportion, the essential indentity of each component.
3. When structure is not obtainable by other metallurgical methods.
4. When components of the desired product cannot be alloyed conveniently, because of excessive spread in their melting points or because of their immiscibility.

Powder metallurgy has certain advantages over other processes and its use is recommended when:

1. Casting and forging are difficult.
2. The usefulness of the product is increased by its purity.
3. The article is adversely affected by cast structures.
4. The article, after casting, requires excessive machining or involves considerable scrap in its manufacture.

II. Theory

Sintering is used in powder metallurgy to express what happens when metal powders adhere by the action of their surface cohesive forces, in practice generally accompanied by the use of high temperature and pressure. There should be no implication of fusion although it may occur in some cases.

A. Degree of contact or porosity is the most important factor in sintering powders. (17)

1. Influence of particle size and shape on porosity
   a. Packing of spheres of equal size. Theoretical porosity is obtained when maximum packing occurs by 1 on 4 arrangement of spheres of equal size. The minimum porosity is 29.95%.
   b. Packing of spheres of unequal size. The porosity increases because packing decreases and approaches a minimum value of 33%. This includes the probability of small spheres passing through the interstices of large spheres. As a restur grain size is important and usually is specified.
   c. Effect of powder shape on packing. Metallurgists agree about the importance of powder shape, but are of diverse opinion as to its effect. Laboratory experiments have shown that spherical particles give a more uniform porosity of minute and uniformly distributed interspaces. Irregular

shapes increase the porosity with a maximum being obtained in needle-like powders. Uniform disc shapes may give decreased porosity.

d. Effect of random packing. Random packing produces irregularities which increases the porosity. This increase is more pronounced in irregular shaped powders.

e. Effect of particle size. Theoretically, the decrease in powder size should have no effect on porosity. It has been found that finer powders have a greater porosity wich is due to larger surface area per unit volume, frictional and electrostatic forces, and bridging.

2. Influence of applied pressure on porosity. Pressure reduces porosity.

a. By movement of particles into voids

b. By deformation of particles so that they key one into the other.

c. By flattening of the microscopic and sub-microscopic roughness on particle surfaces.

Pressure decreases porosity and increases density. Pressure increases the total contact area and increases the cold sintered strength.

3. Influence of temperature on porosity. The following must be considered:

a. The volume effect of gases and vapors. Their solubility increases with temperature and varies as the pressure. Exerta pronounced effect on the properties of the final product, increases hardness, etc.

b. The sintering is aided by causing an increase in plasticity of the metal powder. The different metals have different sintering temperatures.

c. Sintering temperature causes shrinkage which decreases porosity and increases density. Fine powders have a greater shrinkage.

B. Preparation of metal powders (21, 17, 20)

Powder metals can be made by any one of the following methods. The selection of the method depends on many factors such as cost, purity, properties of metal, etc.

1. Machining yields filings, turnings, and cuttings which are usually by-products and serve as reducing agents and constituents in hard-finish cements. Dental alloy powders which are expensive are usually made by this method. The high cost of the product is not materially affected by this expensive method.

2. Milling by stamp, ball, or attrition mills are used for metals like Sb, Bi, Sn, et.

a. Cr, Mn, Mo. Ni, and Ti are powdered in ball mills after a preliminary crushing.

b. Malleable metals, as Cu and Al, are made by stamping or hammering process which produces flaky powders. This is done under some lubricant to prevent their welding together. The copper flakes are used for commutator brushes, and aluminum for pyrotechnics, flares, and liquid O_2 explosives. Largest use is paints.

c. Finely powdered metals which may be explosive, a Al and Mg, are made by the Hall, Hametag or Eddy process.

3. Shotting process produces coarse, rough spherical powders from metals which don't oxidize too readily in air, by allowing molten metal to drop through a screen or small orifices, solidifying in air and dropping into water. Oxidizable metals

are made in an inert atmosphere. Pb shot made in this way usually has a little Sb added to increase the surface tension and make nearly perfect spheres.

4. Granulation process produces coarse metal powders. This process involves rapid stirring of a slowly cooling molten metal. The granules become coated with an oxide. Al, Cd and Zn are made by this method. Granulated Al is used in Thermite process.
5. Atomizing is useful for metals with melting point lower than 700° C. The powder is produced by forcing a stream of metal through an orifice and striking this stream with a blast of air, steam or gas. Rapid chilling prevents excessive oxidation. Al, Zn, and Sn produced in this manner are used for moulding work. Exceptional care must be taken to avoid Sparks, otherwise explosions will result.
6. Condensation of metal vapors is a process used to produce Zn, Fe and Ni.
   a. Distillation of Zn produces a very fine powder which is used for pigments.
   b. Carbonyls of Fe and Ni are produced by passing CO over Fe powder at 100-200°C and 2000-3000 lbs/sq. in pressure. The carbonyl is decomposed between 150-400°C in an atmosphere of N_2, and in a vessel whose walls are maintained at a low temperature. Alloy powders may be made by a joint decomposition of mixed carbonyls. Powders produced are nearly perfect spheres ranging in size from 1 to 10 microns.
7. Reduction of metal compounds is process used to prepare W, Mo. Fe, Co and Ni. Usually the oxide is reduced in an atmosphere of H_2. The size of the powder depends on the size of the oxide particles.
8. Chemical precipitation involves the deposition of one metal from solution by another. Sn from a solution of $SnCl_2$ by Zn and Ag from solution of $AgNO_3$ by Zn are examples of this process. The Ag powder is used to make molded electrical contacts with powdered Cu and graphite.
9. Electrolytic deposition produces powdered metals when the electrolytic conditions are controlled rigidly.
   a. From an aqueous solution, Cu, Sn, Ag, Cd and Sb as a powder can be obtained by use of a high current density.
   b. From a fused salt bath, Th, U, Ta and Cb are obtained as fine powders.
10. Sintering together two metals, one of high melting point and one of low melting point, and maintaining the temperature above the melting point of the low melting constituent will give a diffusion of this substance throughout the mass of the high m.p. member. The resulting mass can then be broken up into a powder. In this manner, master alloys of a high melting element can be diffused in a matric of Cu. Examples are Cu-W, Cu-Cr, and Cu-Ho.
11. Forming an alloy and removing one constituent is employed when a very fine metal powder is desired for catalytic work.
   a. By alloying Ni with molten Al and then dissolving out the Al by a NaOH solution, a very fine Ni powder is obtained.
   b. By amalgamating and distilling off the Hg, an extremely pyrophoric powder is produced which must be stored in an inert atmosphere.

C. Processing from powder to ductile metal. (22) The following procedure describing the production of ductile tungsten can be applied to other metal powders with few changes such as sintering

temperature or applied pressure. When high purity desired WO_3 is reduced by dry H_2; when reduced by C, the W contains a little carbide and the impurities contained in the carbon.

1. Pressing. The powder is pressed in steel dies under hydraulic pressure of 5 to 25 tons per sq.in. The dies measures 1/4 x 1/4 x 8 to 24 inches, and such an 8" bar weighs 90-100 g. Fine powders can be handled successfully, but coarse powders need the addition of a volatile binder - such as glycerine or water.
2. Sintering is accomplished in an electric furnace at 900-1050°C. in an atmosphere of H_2(prevent oxidation). When carbon plates used to support ingot, sintering must be done below 900°C to prevent carbide formation. The ingot obtained is strong, but porous and non-crystalline, has a density of 12 (60% the density of pure W). During this step the binder is volatized off and the resulting ingot is too fragile to be worked.
3. Forming. The ingot is mounted between H_2O cooled contacts and heated by its own resistance. At 1050°C, grain growth begins and is accompanied by shrinkage and the partial elimination of voids. The bar shrinks 17%, and the density increases to 17.5 -18.5. The ingot at this stage is strong but very brittle. The temperature is raised to 1300°C, the ingot becomes ductile, and can be worked and hammered.
4. Swaging. The ingot is worked into a rod by a mechanical hammering process. The swaging machine contains two shaped hammers or dies which are rapidly rotated around the axis of the rod and forced together by cams so as to strike the rod. Swaging started at 1300° C for 1/4" ingot and passes through 23 dies to give wire of 0.8 mm. at 750° C. Wires or sheets may be made by swaging. Production of wire is a continuation of swaging operation, and production of sheet is started after a few swaging operations.

III. Production, Application and Uses.

A. Bearings.

1. Porous Bronze Bearings are made of sintered Cu-Sn powders and the compact is exceedingly porous. These may be impregnated with oils. The advantages claimed are:
   a. Contain 25-40% by volume of oil.
   b. Contains all the lubricant needed for its particular use.
   c. Supplies all oil needed at any speed, and has no loss of oil by leakage or dripping.
   d. When heated, more oil comes to the surface and is reabsorbed on cooling.
   e. Bearing has a measure of ductility and conform to irregular shafts by force fitting.
   f. Especially useful under water, in inaccessible positions, where oil neglect is expected, and with dirty oil because it acts as its own filter.

The bearing is composed of 90% Cu and 10% Sn and has same composition as cast bearings. The powders are prepared electrolytically. At the sintering temperature, the Sn melts and surrounds each Cu particle with a thin film of molten metal which results in a rapid diffusion. The porosity is obtained by admixing certain constituents which volatize and leave cavities during the sintering. This is accomplished by the use of stearic acid. The mixture is pressed hydraulically or mechanically, and heated twice, first at 400° C to melt the Sn; second at 800° to sinter. The bearing are impregnated with oil by heating to 110° and quenched in oil.

2. Bearings of High Tensile and Compressive Strength are made of Cu-Pb alloys. Alloys cannot be made by casting because of the difference in melting point and density of the metals. Although liquid mixtures with less than 38% Pb are miscible, Cu crystals separate from 1083° to 954° (monotectic point) while remaining Pb solidified at 327°C. Formerly Zr, S, Te or Se were added to prevent segregation upon rapid cooling. Results were not very good. Powder metallurgy circumvents melting and casting; provides homegeniety; and gives a higher Pb content. (11)

The usual powder metallurgy scheme of mixing the two powders and sintering was not successful becuase the moment the temperature reached the melting point of the Pb, it melted and settled to the bottom of the mold. To circumvent this occurrence Pb shot was suspended in Cupric acetate solution and solution stirred until no copper left in solution. The Pb shot was obtained with a coating of copper. This powder was sintered in an atmosphere of H_2 at 800° C, and the resulting alloy containing 45-55% Pb can be worked and rolled.

a. Composite bearing that are stronger are made with Cu backing and Cu-Pb working face. (11)
b. Cu-Pb bearings in plastic resins. (8)

B. Cemented Cutting Tools (17, 18, 23, 19, 14, 3)

Although this is limited to carbides chiefly, recently interest has been aroused in the evident possibilities of the borides, nitrides and silicides. This interest can be shown by the number of patents taken out on the following W(C, B, Si), Ti(C, B, N.Si), Ta (C,N,B,Si) Cr(B,C,Si), ZrC, ThC, V(N,B,Si), FeB, CbC, HfC, SiC, BN bonded with a large variety of metals and alloys.

1. Preparation Procedure - illustrated for carbide, but is suited to others by changing conditions (23).
   a. Form the metal carbide in the form of a powder by heating a mixture of carbon and metal oxide or metal for several hours at 1500-2400°C.
   b. Mix intimately carbide powder with binding metal powder.e.g.Co or Ni
   c. Compress the powder mixture in molds at pressures of 15 to 30 tons/sq.in.
   d. Initial sintering is done in an inert atmosphere, H_2, at 800-900°C. This gives the product sufficent strength for handling and forming.
   e. Final sintering is accomplished at higher temperature (1400-1600°C) in an inert atmosphere to diffuse the components and to give a real alloying action.
2. Requirements of hard tool material. (18)
   a. High melting point is not important in itself, but hardness seems to be a concomitant of high melting compounds. Hardness is actually a function of the chemical attraction between atoms.
   b. Simple crystalline structure of high symmetry is desired to permit slippage without breakage
   c. High thermal and electrical conductivity.
   d. Chemical stability under conditions of use.

3. Principle types used at present time (17, 23)
   a. WC with Co etc. are sold as Widia, Carbaloy, Wimet, and Ardaloy
   b. TaC-WC with Co or Ni are sold as Ramet and Tontaloy
   c. TiC-WC or MoC with Ni sold as Tianit and Cutanit

C. Preparation of Ductile Metals, Alloys, and Other Uses.

1. Commutator brushes are made of flaky Cu powder with graphite. Usefulness lies in reduced wear. (20, 21)

2. Copper and Aluminum powder in the form of flakes is used for paints because they have a greater unit surface and when properly orientated in the film give a continuous metal coat. (20, 21)
3. Fe and Ni powders are used extensively to make permanent magnents and magnetic cores.(12) Recently polystyrene and cellulose derivatives have been used as binders for powders to make magnetic cores. (8)
4. Composite Cu-W rods containing 40% Cu are used as welding electrodes. (14)
5. Tungsten for lamp filaments has thorium nitrate added to WO_3 before reduction. Presence of Th prevents grain growth and overcomes off-setting that occurs when filament used in an a.c. line. (13)
6. Tantalum and columbium (ingots) are produced by powder metallurgy in the same manner as tungsten, but all the sintering operations must be made in a vacuum furnace and the powder is produced by electrolysis of fused bath containing K_2TaF_7 or K_2CbOF_5. (4,5,6). Metal used for corrosion resistant equipment and vacuum lamp parts.
7. Uranium is produced by powder metallurgy in a manner analogous to tungsten. Powder obtained by electrolysis of fused salt KUF_5 in $CaCl_2$-NaCl bath or reduction of calcined oxided with calcium hydride. The powder is used to make acid resistant master-alloys of Ni which can be used to alloy with steel, nickel or copper in molten state without loss due to oxidation (3,9)
8. Thorium powder made by electrolysis of fused salt $KThF_5$ in NaCl--KCl bath with a Mo cathode. Metal made from the powder like W and U. The product is used for X-ray targets. (10)
9. Titanium powder and alloys can be made from titanium hydride. Cu-Ti alloy is of interest because 2.58% Ti in Cu imparts additional tensile strength which is retained at high temperatures to a greater degree than other alloys. (1)
10. Zirconium powder made from zirconium hydride. Uses are based on high heat of combustion and low ignition temperature. Used now for ammunition primers and smokless flash powders. (16)

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Inorganic Seminar

November 19, 1940

ABSORPTION SPECTRA OF COORDINATION COMPOUNDS

Apparatus used for determining absorption spectra.

1. Spectograph
   a. Prism instruments of various dispersion and resolving power, and of various material depending upon the portion of the spectrum being investigated.
   b. Grating instruments which now can be considered available.
2. Method of obtaining the rate I_o/I
   a. Visual comparison with the use of a sectorphotometer.
   b. Photographic comparison with or without the use of a sectorphotometer, "spekkerphotometer" or echelon cell
3. Light source
   a. Continuous source such as hydrogen discharge tube for ultraviolet or a carbon arc for the visible
   b. Line source such as the iron arc or spark

Method of recording results: Lambert-Berr law: $I = I_o\, 10^{-\epsilon Cd}$

I and I_o are determined for a number of definite wave-lengths or frequencies. ϵ or a factor of ϵ is plotted against the wave-length or frequency.

x x x x x x x

The absorption spectrum of a large number of coordination complexes is known and many explanations have been proposed as to the origin of the absorption. R. Tsuchida has studied some of these compounds and has put forward a theory which will be discussed.

The metallic complexes have absorption bands which start in the visible and also occur in the ultraviolet. These bands have been designated first, second and third as you go toward the shorter wave-lengths. The first band is attributed to electron transitions in the unsaturated transition shell of the central atom. The shift of this band is attributed to the influence of the field around the coordinated group upon the central atom. The second band may be attributed to the coordination electrons, and is, therefore, the most general characteristic which a coordination compound should possess. The third band is assumed to be due to a pair, or pairs, of negative groups coordinated in trans-positions. There may also be absorption bands which are due to the coordinated groups themselves, these are called special bands.

The order of the hypsochromic effect of the coordinated groups upon the second band gives the order of the strength of the coordinate linkages and is an indication of the stability. The substitution of coordinate groups proceeds in the same order as they produce a hypochromic effect on the second band.

Some coordination compounds may lack the first, the third, or both the bands but the second is always present.

The above conclusions have been drawn from the absoprtion of cobalt coordination compounds. From a study of the chromium compounds it is found that they follow the same rules as the cobalt compounds.

Molecules containing the (NCS) group have a special band due to this group which occurs between the second and third bands. This is why the compound $[Co(NH_3)_5(NCS)](NCS)_2$ was originally thought to be an exception to the third band rule. The chromate ion does not give the first band but does the second and third. Absorption spectra of polynuclear compounds may be analyzed into those of the component complex radicals.

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Ed Dunlop

Inorganic Seminar December 1o, 1
PRODUCTION AND MEASUREMENTS OF LOW TEMPERATURES

Introduction:

Temperatures have always interested man. In the summer it is too hot, in the winter too cold. But what was the extreme of cold obtainable. Was Fahrenheits zero the ultimate? This has always puzzled scientists. Was there an indefinite extent of cold possible?

There were origanally three ways of obtaining low temperatures. Namely, the rapid expansion of a compressed gas, the rapid evaporation of a liquid, or the evaporation of a liquid brought about by absorption of the vapor in a second liquid. The rapid expansion method makes use of the fact that if a gas expands in an insulated system, the temperature of the system drops. Of course, the compression is a heating process, but the compressed gas was always precooled. It was in this type of system that heat exchangers were first used. Mere pumping pf the vapors above a liquid sufficed to cool the liquid by drawing heat from the system. Valuable vapors were condensed and reused. If necessary the vapor was dissolved rather than removed by pumping, vis. the ammonia cycle.

Gas liquifaction:

Scientists have tried to reduce all known gases to liquids. This involved the attaining of lower and lower temperatures. In the course of this work it was found that there was a critical temperature and pressure which had to be attained before the gas would liquify. Liquifaction is used today in all attempts to obtain low temperatures. This work led to the discovery of the Joule-Thompson effect which states that below a certain temperature the expanding of a gas thru a porous plug is a cooling process.

The usual steps in liquifaction of gases is to obtaina pure gas, copress it, and cool it while compressed. Then the gas is allowed to expand, either through a plug (Joule-Thompson) or by doing external work. In all modern systems the cooled gases or liquids are used to further cool the incoming gas. Further ideas which have been adopted in this work include the Cascade system of cooling the incoming gases in a medium more readily liquified, the desorption of gases on active charcoal, and the phenomena of demagnetization at extremely low temperatures.

Temperature measurements:

The temperature scale is based upon two fixed points, and a number of equal divisions between those points. In the centigrade scale the freezing point is 0, the boiling point 100. This sets the size of a unit. Any property of any substance which depends on or varies with the temperature according to some known law, may be used as a thermometric indicator. Thus we have the expansion or contraction of a solid, gas, or liquid, or the vapor pressure of a liquid, or the electrical resistance of a wire, or the thermoelectric electromotive force set up at the junction of two dissimilar metals.

PRODUCTION IMPROVEMENTS OF LOW TEMPERATURES

Introduction:

Temperature has always interested man. In the summer it is too hot, in the winter too cold. But what was the extreme of cold obtainable. The Phenomenon zero the ultimate? This is a question worthwhile considering. Was there an instructive extent of cold possible?

In the ancient ordinarily three ways of obtaining low temperature. Namely, the radiation of a coolness, the evaporation of a liquid, or the evaporation of a liquid about by absorption of the vapor in a cool liquid. The radiation method was of the first that it is used in an insulated system, the temperature of the system. Of course, the compression is a modern process, but compressed gas is always produced. It was in this type of system that exhausters were first used. The pumping of the vapors above a liquid suffered to cool the liquid by drawing heat from the system. Volatile vapors were condensed and removed. It necessary the vapor was dissolved rather than removed by pumping, via, the ammonia cycle.

Liquification:

Scientists have tried to reduce all known gases to liquids. This involved the attainment of low and low or temperature. In the course of this work it was found that there were critical temperature and pressures which had to be attained before the gas would liquify. Liquification is usually lowering of obtain low temperatures. This work led to the discovery of the Joule-Thomson effect which states that below a certain temperature the temperature of a gas flow a porous plug is a cooling process.

The way I sees in liquification of gases is to obtain pure gas, compress it, and cool it while compressed. Then the gas is allowed to expand, either through a plug (Joule-Thomson) or by doing external work. In all modern systems the cooled gases or liquids are used to further cool the incoming gas. Further ideas which have been adopted in this work include Gaseous mixture of coolers, the inert gases in a mixture, reversibly liquified, the application of gases on cooling a gas and the phenomena of [illegible] liquification of [illegible] low temperature.

Temperature measurements:

In temperature measurements based upon the fixed points, no number of equal divisions between those points. In the measurements the Fahrenheit scale is, the boiling point 100. This depends on or varies with [illegible] of any substance [illegible] known. Hg be used as a [illegible] according to [illegible] have the [illegible] or contraction [illegible] Thus on [illegible] or the vapor pressure of [illegible] gas, or liquid, of a [illegible], or the thermoelectric [illegible] electrical resistance [illegible]

The most valuable fundamental means of measureing temperatures is by means of a gas thermometer, which depends on the variation of either pressure or volume at constant volume or pressure, as the temperature changes. This of course is only valuable when the gas does not tend to liquify. This is then correlated with an International Scale, which defines certain specific points, and the means of calibrating between the points. The fixed points are known as the oxygen, ice, steam, sulfur, silver and gold points. Resistance thermometers are used in the various ranges.

Below the oxygen point the temperature scale has not been set on an international basis yet, but points have been determined which bring the useful ness of the scale to the boiling points of Hydrogen and Helium. Below $1^{o}K$ additional factors come in which make a temperature scale more complicated.

Peter M. Bernays

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MANGANESE

I. Strategic Metals

A strategic material is classed as one which is not available in the United States in sufficient quantity to meet the needs of a rearmament program - large quantities must be imported. Such materials may be regarded as strategic even in peace time, since the cutting off of a supply of any of them would interfere seriously with domestic manufacture and needs.

The number of metals that might be placed in the strategic class from a military or preparedness point of view is large but the Army and Navy Munitions Board has designated Mn, Cr. Ni, Hg, W, Sb, and Sn as the more important strategic metals.

Despite the fact that these metals represent only a small percentage of the national metal requirements, by virtue of their strategic classification - i.e. national deficiency adequate provision for national defense can tolerate no deficiency, however small.

II. Strategic Importance of Manganese

Manganese is ranked by many authorities as the United States No. 1 strategic material. It has been estimated that approximately fourteen pounds of manganese are used in making every ton of steel. The mineral is consumed in the form of ferromanganese containing about 80% metallic manganese and the remainder iron and carbon. No equally-efficient substitute for ferromanganese has ever been successfully developed.

Since the World War (No.1) the United States has been forced to import more than nine-tenths of its consumption of ferro-grade ore. The great bulk of this ore has come from such far-off sources as Russia, leading world producer, India and African Gold Coast while the somewhat safer sources of Brazil and Cuba have contributed only relatively small amounts.

III. Domestic Supply

The manganese oxide deposits of Philipsburg, Montana and the rhodochrosite ($MnCO_3$) and oxide deposits at Butte, Montana have been the major sources of supply of manganese ore of a grade approaching ferromanganese ore specifications. Much smaller tonnages are derived from Virginia, California, Arkansas, Arizona, and Georgia in the order named.

Domestic Production of metals in 1937

Production	Approximate production, tons	Percent from domestic ores
Pig iron	36,000,000	96.7
Primary copper	820,000	92
Primary slab zinc	557,000	99
Primary lead	467,000	95
Manganese (ferro-)	300,000	1.4
Primary aluminum	146,000	33

Manganese deposits are broadly distributed throughout the United States but the low-grade deposits are available in greatest abundance.

IV. Electrolytic Manganese

The electrolytic method for producing manganese metal will no doubt have a direct bearing on the present strategic position of manganese since it offers a method for utilizing the great tonnages of low-grade American ores. Electrolytic manganese had its inception in the Bureau of Mines. The Electro Manganese Corp. undertook to commercialize this work in Oct. 1938, and a plant at Knoxville, Tenn., designed to produce five thousand pounds a day was completed in May 1939. Total production to date has been three hundred thousand pounds of 99.9% manganese pure metal which has been consumed entirely in the non-ferrous industry.

V. Uses of Manganese

As previously noted nearly all of the manganese consumed in this country goes into the steel industry. The introduction, however, of electrolytic pure manganese at a relatively low cost opens a new field in which manganese may be used as a base metal in both ferrous and non-ferrous alloys. Some of the alloys being investigated at the present time are Mn-Cr, Mn-Ni-Cu, Mn-Cu-Zn, Mn-Al and the Mn-Fe-Cr alloys.

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Reported by R. C. Gunther
December 17, 1940

A NEW CLASS OF COMPOUNDS OF POSITIVE MONOVALENT IODINE

Salts which are derivatives of the very labile base, IOH, have been stabilized by the formation of co-ordination compounds with pyridine. These compounds are prepared by the action of iodine on a silver or mercurous salt in the presence of pyridine or a non-aqueous solution of pyridine. Representative equations:

$$AgNO_3 + 2\ py + I_2 \xrightarrow{CHCl_3} I(py)_2\ NO_3 + AgI$$

$$HgOOC.C_6H_5 + 3\ py + 3I \longrightarrow HgI_2.2\ py + I(py).OOC.C_6H_5$$

The following compounds were prepared:

$[I(py)_2]NO_3$ and $I(py)NO_3$
$[I(py)_2]ClO_4$
$I(py).OOC.CH_3$
$I(py).OOC.C_6H_5$
$I(py).OOC-C_6H_{11}$
$I(py).OOC-C(C_6H_5)_2CH$
$I(py).OOC.CH_2$
$I(py).OOC.CH_3$
$I(py).OOC-C_6H_5$
$I(py).OOC-C_6H_4$
$I(py).OOC-C_6H_4-NO_2$

The iodine in these compounds bears a positive charge as evidenced by its chemical behavior, and by its deposition at the cathode when the compounds are electrolyzed in non-aqueous solvents.

Conductivity measurements do not give definite evidence, but it is probable that the compounds are of the types

$$[I\ py_2]\ X \quad \text{and} \quad [I\ py_x]$$

Decomposition of the compounds with equivalent quantities of alkali yields the oxide, $\begin{matrix} I(py) \\ I(py) \end{matrix}\Big\rangle O$, which gives up pyridine readily to form $\begin{matrix} I(py)_2 \\ I(py)_2 \end{matrix}\Big\rangle O$. The latter disproportionates to give $I(py).IO_3$.

Hydrolysis first yields I(py)OH, which in turn breaks down to give iodine and $Py.HIO_3$.

The I-py compounds react with alkali halides to form I^+- halides or their pyridine addition compounds. Reactions with metals show that the iodine in these compounds probably should be placed with the noble metals in the Electromotive Series. However more work must be done before its place can be assigned with certainty.

Abstract of UBER EINE NEUE KLASSE VON VERBINDUNGEN DES POSITIV EINWERTIGEN IODS

Heinrich Carlsohn
Verlag von S.Herzel inLeipzig (1932)

J. Kleinberg
Feb. 11, 1941

Inorganic Seminar Feb. 18, 1941

Geometrical electron optics - The electron microscope.

Probably the most interesting portion of the history of science deals with penetrating the world of the infinitely small. For many centuries it has been known, even to the time of the Greek philosophers, that all matter could be subdivided into small and smaller particles. It was left to the inventive genius of man to begin the investigation into this realm. Possibly the discovery of some transparent stones, which caused a magnified image, led to the first magnifying glass. Very slowly the science of optics developed and in the 17th century the first microscope was put to use. From this point the advancements in medicine, bacteriology, and other branches of the natural and physical sciences were phenomenal, and beyond the scope of this discussion.

Limitations of visual instruments.

As the microscope became more and more generally used and refined it became evident that the ultra-small was not within reach of man-mad instruments, even in the realm of living organisms, at least in the range of visual light. Toward the end of the 19th century the reason for the limitation was revealed with, undoubtedly, somewhat of a shock since it spelled the end of development in microscopy. This "scientific bottleneck" was due to the very means of observation-light The modern microscope is as fine an instrument as is possible to construct using visible light as a source. The limiting factor is not the amount of possible enlargement, but is the resolving power. This is simply the power of an instrument to discriminate between two minute objects that lie close together. It depends on the wave length of the light used, the refractive index of the object space, and the angle of the cone light emanating from the object and used by the objective to form the image. The refraction index can be increased by the use of immersion fluids; the angle of cone light, by improving the lense system; the wave length of light can be reduced by using ultra-violet instead of visible light. All these increase the resolving power but the limit of discrimination is still above 0.1 micron.

Attempts to go beyond the limitations of visible light.

Many ingenious indirect methods have been developed to explore the world beyond the limits of the microscope. One of these is the ultra microscope which reveals the presence of particles below the resolving power of the microscope. This however tells nothing of their size and shape. They are rendered visible due to the scattering of light. When the particles are in Brownian movement a twinkling effect occurs as a particle periodically enters the focal plane of the microscope objective. In viscous colloidal solutions, the Brownia motion can be largely eliminated thereby permitting counting of the particles as points of light in a dark field. One of the greatest contributions of ultramicroscopy has been its ability to reveal partic in count methods.

In these counting methods the individual dispersed particles are revealed, counted and their equivalent average diameter calculated from known values of the density and weight of the material in the dispersed phase. This gives an approach to size and shape but still is far from a refined visual method of observation.

X-ray diffraction methods, utilizing extremely short wave lengths in the radiation spectrum will reveal certain aspects of matt as to its crystalline or amorphous nature, however even though certain facts are obtainable as to atomic distances and crystal structure the

ultimate shape does not necessarily follow. The whole realm of polymers, bacteria, or dispersions in colloidal systems is not benefitted by X-ray methods. We must conclude thatnone of the above attempts at refinement take the place of good visual observation.

The concept of electron or geometrical optics

Within the past few years a new branch of physics has been developed known at present by the name of "electron optics" or"geometric electron optics". It is based mainly on the recognition of analogies in the behavior of light and electron beams. This analogy closely allies the photon conception of light rays and the consideration of the electrons as particles having wave nature, the wave length of which is a function of the electron velocity. It has been known for fifty years that cathode rays (beams of electrons) travel in a straight line in the absence of any matter or field; that they can be concentrated in certain cases; that an electromagnetic field deflects such rays. Electron optics have found useful application in radio tubes and particularly in television tubes. An interesting comparison is the electron gun used in television with an optical analog. As can be mathematically demonstrated there exists a close resemblance between the action of a magnetic or electric field of rotational symetry on an electron beam and the action of a glass lense on a light beam. The science of electron optics is based on the above principles.

For electron velocities between 30,000 and 100,000 volts, the wave length is 1/100,000 that of the wave length of visible light. With such wave lengths optical systems are at hand with incomparably better resolving power with no limitations even to atomic dimensions. No instrument using electron optics is perfected to this point but we are allowed to go some fifty times further than the best imaginable light microscope. The useful limit of the light microscope is about 2000--electron optics will give 100,000 as a useful limit of magnification.

The electron microscope.

A high power electron microscope for observation by transmission is constructed with the same essential elements as a light microscope. The object is "illuminated" by a beam of electrons which are emitted from a hot tungsten cathode and accelerated to high velocities by a field of 30-60,000 volts. The electron beam may be concentrated by means of a magnetic condenser lense, this, serving the same purpose as the substage condenser of the microscope.

The electrons passing thru and around the object are focused by the magnetic field of the second solenoid in an image plane at about 100 diameters magnification. Following the analogy of the light microscope, the second solenoid is called an objective lense. The primary image must be magnified further in order to render the finer detail visible to the eye. The variations from the light microscope in the stage apparatus becomes evident when it is noted that the whole electron path, lense system, object, etc. must be maintained in a high vacuum of 10^{-4} to 10^{-5} mm. Hg in order that the electrons will not be scattered or destroyed by molecules of gas, leading to a distortion of the image. The electron beam is finally focused on a fluorescent screen as a real image, viewed by a binocular system.

The currents controlling the magnetic field strength in solenoids must be maintained at constant values during a photographic exposure, otherwise drifts of the image occur. The resolving power

depends, besides the above considerations, on the thickness of the object to be examined. The object cannot be mounted on slides but instead extremely fine nitrocellulose membranes are used, thereby reducing the interference and scattering to a minimum.

The R.C.A. electron microscope is soon to be added to the instrumental collection of the analytical division of the University of Illinois. This instrument is undoubtedly the best of its kind and will place this institution in the select group of some four or five institutions and laboratories with a first grade instrument.

Magnifications from 1500 to 35,000 are obtainable but the defination in the photographs (obtained by replacing the fluorescent screen by the sensitized plate) is sufficiently fine to give a final magnification of one or two hundred thousand times. Specimens and photographic plates are easily and quickly interchanged with out breaking the vacuum of the main body of this instrument. This is accomplished by a cleverly designed system of "air-locks". The mechanical nature of this system is so exactly constructed that the object may be removed to the secondary chamber, additional experiments carried out and finally replaced to the original position with little or no change in focus, obtaining identical fields. The chromatic abberation of the RCA instrument has been reduced to such a point that exposures of five minute duration can be made.

Uses and possibilities of the electron microscope.

When it is realized that the degree of magnification would make an average human hair appear to have the dimensions of a California Giant Redwood tree, the possibilities seem limitless.

The shapes and sizes of colloidal particles have been clearly defined down to some 30 A. This is well within the limits of molecular dimensions in modern plastics and polymers such as the poly-vinyl type. The function and nature of carbon black filler in rubber and latex has been revealed. Graphite platet structure was picked up at 50,000 diameters. Other fillers such as ZnO and $BaSO_4$ also show individual platets. Lyophobic gels and sols have been studied particularly in comparison with X-ray methods. Some interesting fiberous structures of iron and nickel were obtained by decomposition of the Fe and Ni carbonyls. In bacteriology the internal structure of many organisms heretofore not even observed have been clearly revealed. Important facts may be uncovered concerning the action of catalysts, the action of chemicals on bacteria of disease to show how the drug actually killed the germ.

The limitations of such an instrument in modern science are left to the reader.

Robert C. Brasted

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I. Removal of Soluble Silica From Water By the Hot and Cold Methods.

A. Removal of silica from water by the cold method.

General introduction: Silica in water is of two types, colloidal or suspended, and crystalloidal or dissolved. The cold and hot methods deal with the removal of the crystalloidal silica. These processes are external or carried out prior to the use of water in boilers to prevent scale formation. In the cold process aluminum hydroxide was used. This was used in different forms, such as freshly precipitated, dry powder (C.P.), dried at 105°C. from fresh precipitate, and commercial sherry.

Conditions of tests:

Three liters of water were used in each case. Varying temperatures were used, but in higher temperatures, the reagents were added before the higher temperature was reached. Each reagent was added separately, and stirred constantly during retention to keep precipitates in suspension. The water was prepared synthetically and calcium was the only kind of hardness used. Analyses were made immediately and in no case did the water stand in glass over 1-2 hours before being acidified for Silica determination. Colorimetric determination was made with a Taylor analyzer. Silica was determined gravimetrically by the usual method.

Results:

1. The removal of silica by aluminum hydroxide is more efficient at lower temperatures (23°C).
2. Retention of the water for several hours has very little advantage over retention for one hour.
3. Aluminum hydroxide works well in conjunction with the lime-soda method for softening. Aluminum hydroxide is an excellent coagulant, and slightly decreased the alkalinity of the water.
4. The best pH value for the cold method is 7.6-8.0. If pH is above 8.3 residual aluminum will be present in amounts enough to cause analcite scale.
5. Freshly precipitated aluminum hydroxide is the most efficient form. C.P, dried aluminum hydroxide, and commercial sherry are inefficient.
6. Aging of precipitate reduces silica removal.
7. Absorption seems to be the best explanation of the removal of silica by aluminum hydroxide.

B. Removal of silica from water by the hot process.

Conditions of tests:

Three liters of water were used and heated to desired temperatures. At the proper temperature, the reagents were added. Analysis of treated water in each case was conducted on a sample filtered at the temperature of the test. Magnesium oxide was employed in this hot process of silica removal.

Results:

1. Increase in temperature increases the efficiency of silica removal by mangesium oxide (95° best).
2. Magnesium oxide can be used in the same container or softener as lime and soda ash and greatly increases the removal of silica.

3. Magnesium carbonate can be employed in the process but with less efficiency than the oxide.

4. Best pH for low silica content is 10.1. Sodium hydroxide decreases the silica content up to 10.1 and then increases it considerably.

5. The most effective forms of magnesium oxide are the U.S.P. light oxide and "Remosil".

6. The mechanism of the silica removal is not the formation of magnesium silicate, but more possibly a complex of magnesium hydroxide - magnesium silicate.

7. Results in actual plant operations indicate there is greater efficiency in silica removal by this process than in the laboratory.

II. Vitreous Silica Equipment

A. Vitreous silica equipment in chlorination processes.

Introduction: An extension in the use of vitreous silica has come about in organic chlorination and inorganic chlorodizing. Chemical reactions involving chlorine entail unusual problems of photochemistry, catalysis, temperature, and resistance.

Suitability of vitreous silica:

Quartz glass and fused silica are identical in homogeneity and chemical properties, and similar in thermal, catalytic, and other physical properties.

The clear grade is unusually transparent in the ultra violet range, transmitting down to 2000 A.

In chlorodizing practice, chlorine has no effect on the silica equipment up to 1400 C. One exception is in fused lithium chloride which is active in dissolving silica.

Fink and de Marchi found that sulfur compounds react with silica especially around their dissociation temperatures.

Chauvenet found that the nascent chlorine liberated from phosgene during decomposition caused no reaction with silica.

Vitreous silica can be used safely up to its crystallization temperature, 1000-1100 C. Reducing gases accelerate the devitrification at the upper temperature, while sodium tungstate and potassium chloride affect the lower temperature (300)

The thermal conductivity is excellent and increases with rising temperature. The linear coefficient is smaller than any other manufactured product and is practically constant with changes in temp.

Vitreous silica is inert and non-catalytic, although it can be a catalytic carrier.

On account of its high electrical resistance it can be used for insulating current leads and arcs.

Chlorodizing reactions:

Apparatus for inorganic reactions of chlorodizing must necessarily withstand higher temperatures than organic chlorinations. Production of $AlCl_3$ requires 1000°C; $BeCl_2$ - 800°; $ZnCl_2$-600°. Separations of metal chlorides by heating ores has been carried out at 1100° in separating Iron, chromium, and nickel.

Phosgene undergoes decomposition above 300°, or by radiation of wave length 2750-3050A.

Wohlers described an electrically heated fused silica rotary furnace for producing anhydrous metal chlorides. Richardson suggests that steam be used in a tubular furnace for making these chlorides.

Backerville recommended vitreous silica tubing for chlorodizing thorium oxide with carbon

The preparation of very pure metallic chlorides often involve fusion or dehydration which is carried out with a current of HCl in a silica boat inside a silica tubing.

Photochemical reactions and applications

Ultra violet light brings about molecular rearrangement in chlorinating hydrocarbons, and organic halogen-sulfonates. 3132A or below seems most effective. If short wave length is desired a low-pressured mercury vapor lamp in quartz (2536A region) is advantageous because of its low temperature. Where full actinic power is desired, fused quartz should be used.

B. Chemistry and Vitreous Enamels

Vitreous enamel is a silicate coating that has been fused onto a metal base. Progress in vitreous enameling was slow because of the poor quality of castings.

Sheet iron base:

The carbon content of steel must be under 15% to prevent blistering of the enamel. Fusion welding has made it possible that whole articles such as refrigerator bodies can be made as a unit. In arc welding the bare electrode must be covered to protect it from the atmosphere. This is used on parts used on heavy stock. Irons that anneal readily so that the resulting gases pass off before fusion of the enamel, give satisfactory results. The presence of hyperentectoid cementite causes blistering. Stabilized pearlite can be used successfully. For stove pipe the carbon equivalent should be 4.3 and is computed by this equation:

$$C.E. = \frac{\% Si + \% P}{3} + \% \text{ carbon}$$

Enamel Compositions:

Raw materials used are soda ash, sodium nitrate, borax, and oxides of tin, lead, and zinc. Antimony and zirconium compounds have been used as substitutes for tin oxide as a white pigment and opacifier. Barium carbonate has been substituted for lead oxide in wet-process cast iron enamels.

Consistency of enamel slips:

The slip must be of a high degree of consistency in order to produce a smooth, even coat. Enamel slips follow the laws of plastics rather than viscous flows. The use of a plastometer enables the operator to establish graphs corresponding to correct consistency for the slip.

Adherence: Cobalt oxide is used in the ground coat to insure adherence. Nickel and manganese oxides are used with cobalt oxide, the former is used for adherence and the latter for widening the firing range.

One theory explains that metallic dendrites are formed which X-ray studies indicate are alpha iron, cobalt, and nickel.

Another theory suggests that adherence is due to iron oxide films at the interface between metal and enamel. This ferrous phase, which is approximately 3×10^{-5} inches thick holds the enamel rigidly to the iron.

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Edward Lemon

TABLE I. REMOVAL OF SILICA BY ALUMINUM HYDROXIDE

Analysis of original sample, p.p.m.

Hardness as $CaCO_3$	45
P alkalinity as $CaCO_3$	0
M alkalinity as $CaCO_3$	18
Silica as SiO_2[a]	23.9

Conditions: 2-hour stirring and retention time, temperature 20° C.

$Al(OH)_3$, Dry basis, added in slurry form P.P.M.	Silica Removed as SiO_2, P.P.M.	Analysis of Treated Water: Silica as SiO_2[a]	Hardness as $CaCO_3$	P alkalinity as $CaCO_3$	M alkalinity as $CaCO_3$	pH of Treated Water
25	9.5	14.4	42	0	26	6.9
50	11.8	12.1	42	0	20	7.1
80	20.7	3.2	34	2	44	6.3
100	21.4	2.5	40	0	32	7.1
200	21.6	2.3	40	0	23	7.1

[a] Silica determined gravimetrically.

TABLE II. EFFECT OF TEMPERATURE

Analysis of original sample, p.p.m.

Hardness as $CaCO_3$	44
P alkalinity as $CaCO_3$	0
M alkalinity as $CaCO_3$	24
Gravimetric silica as SiO_2	20.0

Conditions: 800 p.p.m. aluminum hydroxide (dry basis) added in slurry form, 40 p.p.m. sodium hydroxide added, 1-hour retention and stirring time.

Temperature, °C.	Silica Removed, P.P.M.	Analysis of Treated Water, P.P.M.: Silica as SiO_2[a]	Hardness as $CaCO_3$	P alkalinity as $CaCO_3$	M alkalinity as $CaCO_3$
23	19.0	1.0	48	4	40
30	18.5	1.5	52	4	46
50	19	2.0	52	4	40
70	16	4.0	56	4	44
96	11	9.0	80	4	44

[a] Silica determined colorimetrically except on original sample.

TABLE [illegible]. [illegible] COMPOSITION AND
[illegible] SILICA [illegible]

[illegible] of original sample, p.p.m.
[illegible] as CaCO3 [illegible]
[illegible] as CaCO3 [illegible]
[illegible] as CaCO3 [illegible]
[illegible] silica as SiO2 [illegible]

[illegible]: acid-soluble lime and some carbonate, treatment [illegible]

Sample No.	$Al(OH)_3$ Gel Added in Slurry Form P.P.M.	CaCO3 Added P.P.M.	Silica as SiO_2	Calcium as CaCO3	% alkalinity as CaCO3	% alkalinity as SiO_2
			Analysis of Treated Water			
1	0	0	10	[illegible]	[illegible]	104
2	0	0	10	[illegible]	[illegible]	[illegible]
3	50	0	6.0	[illegible]	[illegible]	[illegible]
3	100	0	4.0	[illegible]	[illegible]	[illegible]
4	100	0	4.0	[illegible]	[illegible]	[illegible]
4	100	10	2.0	[illegible]	[illegible]	[illegible]
5	100	20	[illegible]	[illegible]	[illegible]	[illegible]
1	200	0	1.0	[illegible]	[illegible]	[illegible]
2	200	10	1.0	[illegible]	[illegible]	[illegible]
3	200	20	1.0	[illegible]	[illegible]	[illegible]
4	200	0	1.0	[illegible]	[illegible]	77
4	200	10	1.0	[illegible]	[illegible]	75
5	200	20	1.0	[illegible]	[illegible]	[illegible]
5	200	30	1.0	[illegible]	[illegible]	[illegible]
6	[illegible]	40	1.0	[illegible]	[illegible]	[illegible]

Silica determined colorimetrically except on original sample

TABLE V. EFFECT OF TEMPERATURE

Analysis of original sample, p.p.m.:

Hardness as $CaCO_3$	28
Phenolphthalein alkalinity as $CaCO_3$	0
M alkalinity as $CaCO_3$	16
Gravimetric silica as SiO_2	25.0

Conditions: 15-minute retention and stirring time, 200 p.p.m. magnesium oxide added, 40 p.p.m. sodium hydroxide added

Temp. °C	Analysis of Treated Water, P.P.M. Silica as SiO_2*	Hardness as $CaCO_3$	P alkalinity as $CaCO_3$	M alkalinity as $CaCO_3$
30	15	88	70	108
50	6	72	60	100
70	5	60	40	97
90	4	28	30	99

* Silica determined colorimetrically except on original sample

TABLE VI. EFFECT OF pH AND ALKALINITY

Analysis of original sample, p.p.m.:

Hardness as $CaCO_3$	34
P alkalinity as $CaCO_3$	0
M alkalinity as $CaCO_3$	34
Silica as SiO_2*	21.3
pH	7.1

Conditions: 100 p.p.m. magnesium oxide, temperature 82° F., 15-minute retention and stirring time

pH	NaOH Used, P.P.M.	Analysis of Treated Water, P.P.M. Silica as SiO_2*	Hardness as $CaCO_3$	P alkalinity as $CaCO_3$	M alkalinity as $CaCO_3$
9.7	0	1.8	104	18	98
9.6	8.2	1.5	104	40	116
9.3	20	1.4	110	48	120
9.7	40	1.2	84	80	89
9.1	60	0.7	44	88	92
9.9	80	1.3	34	90	148
9.8	100	3.9	34	98	154

* Silica determined gravimetrically

Inorganic Seminar March 11, 1941

Fluorination of Phosphorus Halides

An apparatus and technique have been devised to demonstrate that the fluorination of PCl_3 is stepwise. It has also been shown that the threshold fluorinating temperature lowers with the replacement of chlorine atom by fluorine. In a stepwise reaction the probability of excessive fluorination is minimized by maintaining the reaction zone at such temperature that the unfluorinated liquid will be gently boiling and refluxing at the pressure maintained in the system.

The development of an apparatus and technique for the controlled fluorination of inorganic non-polar halides has made possible the preparation of two new chlorofluorides of phosphorus. Three methods have been used.

A. The Swarts reaction between PCl_3 and SbF_3 in the presence of $SbCl_5$ as a catalyst. With an absolute generator pressure of 250 mm. and a temperature of 39°C. 3.5 hours were necessary to complete the reaction. Analysis of the product gave 58% $PFCl_2$, 19% PF_2Cl and 22% PF_3.
$PFCl_2$ was fluorinated at a pressure of 250 mm. and a temperature of - 15°C. 2.5 hours were necessary to complete the reaction and analysis of the product gave 64% PF_2Cl.
PF_2Cl was fluorinated at a pressure of 720 mm. and a temperature of - 50°C. Three hours were required to complete the reaction.

B. The calcium fluoride reaction, a gas-solid reaction between PCl_3 vapor and hot CaF_2. This reaction was used only with conditions favoring the formation of $PFCl_2$.

C. The equilibrium reaction between PF_3 and PCl_3 to give PF_2Cl and $PFCl_2$. At 250 degrees no appreciable reaction took place, but phosphorus deposits due to a side reaction; at 400° no phosphorus deposited and conversion was about 30% per pass. The pressure used in all cases was 720 mm. Side reactions with the glass tube gave POF_3 and SiF_4 which are difficult to remove from the PF_2Cl. (No attempt was made to find a substitute for the glass reaction tube).

500°, ...ontakes place, but

The products were purified by fractional distillation and then analyzed. The percent chlorine and the percent phosphorus were determined directly, the fluorine was determined by difference. The average of the experimental results for each element differed from the percentage indicated by the formulas by no more than eight parts per thousand.

$PFCl_2$ is stable when stored under pressure in a sealed tube. It is absorbed very rapidly by NaOH solution, evolving heat. Normal boiling point is 13.85°, melting point is - 144.4, latent heat of evaporation is 5950 cal./g.mole. Critical temperature 189.88, critical pressure 48.99 atm.

PF_2Cl hydrolyzes less rapidly than $PFCl_2$. PF_2Cl is stable in a sealed tube at -78 . Normal boiling point is -47.3°, melting point is -164.8°, critical temperature 89.17°, critical pressure 44.6 atm., latent heat of evaporation 4200 cal./g. mole.

Phosphorus tribromide has been fluorinated by two methods which are similar to the first two given for the fluorination of phosphorus trichloride.

A. Reaction between PBr_3 and SbF_3 with bromine as a catalyst. The fluorination was carried out at different temperatures. The best yields were obtained at 170° and 250 mm. This fluorination gave by volume $PFBr_2$ 40%, PF_2Br 40% and PF_3 20%.
Fluorination of $PFBr_2$ was carried out at 0° and 20 - 30 mm. The product was chiefly PF_2Br, but only 25% of the material was converted. Increasing the temperature increased the yield but the percent of the trifluoride was increased.

B. CaF_2 at 140° reacting with PBr_3 with the pressure maintained at 20 mm. 36 hours were required to produce 30 cc. This on distillation yielded 15 cc. of PF_3, 10 cc. $PFBr_2$ and 5cc of PF_2Br.

The fluorination of phosphorus tribromide, like the fluorination of phosphorus trichloride, is stepwise.

$PFBr_2$ can be distilled at atmospheric pressure, but on standing it slowly decomposes into PF_3 and PBr_3. $PFBr_2$ hydrolyzes on contact with moist air, reacts with mercury liberating phosphorus and combines with bromine forming an unstable reddish brown solid which is presumably PBr_4F. The normal boiling point of $PFBr_2$ is 78.4, melting point -115°.

PF_2Br stored at -78° decomposes at the rate of about 1% per day. It hydrolyzes on contact with moist air, reacts with mercury liberating phosphorus and combines with bromine forming pentavalent fluobromides. The normal boiling point of PF_2Br is -16.1°, melting point is -133.8°.

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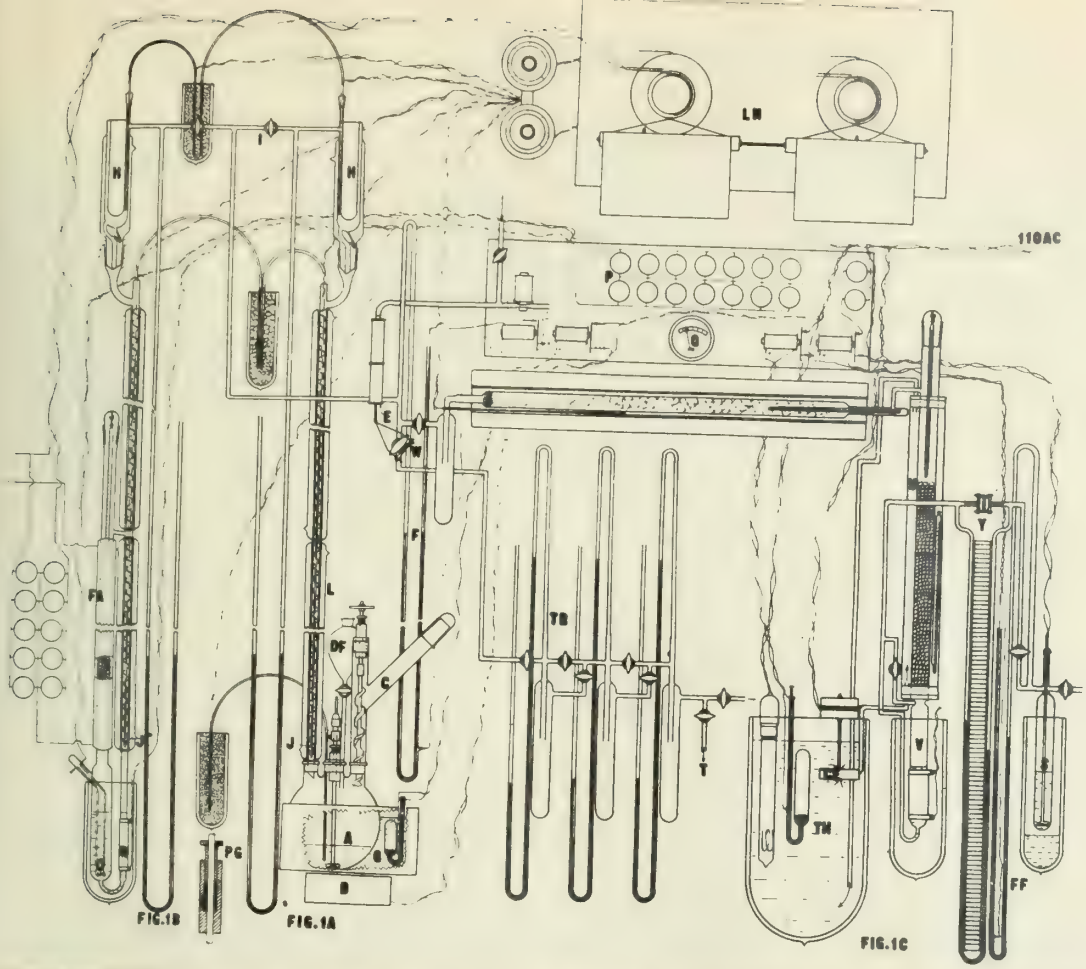
H. C. Eshelman



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ly from neutral solutions of potassium iodide, but readily oxidizes ferrous iron to the ferric state. Perdisulfuric acid is formed in the anode compartment when sulfuric acid is electrolysed at high current densities.

$$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$$

It reacts with water slowly: $H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$

$$\xrightarrow{H_2O} H_2SO_4 + H_2O_2$$

or with hydrogen peroxide: $H_2S_2O_8 + H_2O_2 \longrightarrow 2H_2SO_5$

The structure has been elucidated by d'Ans' and Friederich's syntheses from hydrogen peroxide and two mols of chlorosulfonic acid.

$$2\ ClSO_3H + H_2O_2 \longrightarrow HSO_3 . O_2 . SO_3H + 2HCl$$

Crystallographic studies of potassium persulfate bear out this structure.

Permonosulfuric or Caro's acid, $H_2SO_5HOSO_2OOH$, is formed as indicated above by the action of water or hydrogen peroxide on perdisulfuric acid. In contrast to the perdisulfuric acid, Caro's acid immediately liberates iodine from neutral solutions of potassium iodide. It is recognized as a true peracid by its failure to reduce permanganate. It behaves as a monobasic acid, the perhydroxyl apparently being only weakly acidic. The perhydroxyl group can be benzoylated giving a monobasic acid. Friederich and d'Ans perpared this acid (Caro's) by the reaction: $ClSO_3H + H_2O_2 \longrightarrow HOOSO_3H + HCl$

A. Simon has verified the accepted structure of permonosulfuric acid by Raman spectra measurements.

The action of hydrogen peroxide on sulfates forms addition

Peracids and Persalts.

The so-called "per" acids and salts show differing behavior toward acidified potassium permanganate solution. Some reduce permanganate in the same manner that hydrogen peroxide does; other peracids fail to give this reaction. It has been shown that, in those cases where the potassium permanganate is reduced, the compound is merely a hydrogen peroxide addition compound, i.e. contains H_2O of crystallization, and is not a true peracid. The true peracids contain a peroxy bridge (-O-O-) or a perhydroxyl group (-OOH), and do not as a rule reduce permanganate solutions. However these are not always easily distinguished since the peracids hydrolyse at varying velocities to give the normal acid and hydrogen peroxide.

Peracids and persalts are usually made by electrolysis (anodic oxidation) or by treatment of the acid or salt with hydrogen peroxide or an alkali metal peroxide. These reactions may lead to the formation of either true percompounds or the perhydrate, depending on the acid radical used. The valence of the central atom is not changed in the formation of percompounds by these methods.

Probably the oldest known and the best characterized of the peracids are the two persulfuric acids.

Per (di) dulfuric acid, $H_2S_2O_8$ (HOO_2SOOSO_2OH) is a dibasic acid with extremely high oxidizing power (slowly chars solid paraffin). It does not reduce permanganate solution. It liberates iodine only slowly from neutral solutions of potassium iodide, but readily oxidizes ferrous iron to the ferric state. Perdisulfuric acid is formed in the anode compartment when sulfuric acid is electrolysed at high current densities.

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$$2\ ClSO_3H + H_2O_2 \longrightarrow HSO_3 \cdot O_2 \cdot SO_3H + 2HCl$$

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A. Simon has verified the accepted structure of permonosulfuric acid by Raman spectra measurements.

The action of hydrogen peroxide on sulfates forms addition

compounds:

$$Na_2SO_4 + H_2O_2 \rightleftharpoons Na_2SO_4.2H_2O_2.H_2O$$

These are not true percompounds and exhibit, in solution, only the reactions of hydrogen peroxide.

Percarbonates.

Percarbonic acid can be prepared by anodic oxidation, the reaction being comparable to that involved in the formation of perdisulfuric acid: $2HCO_3^- \rightarrow H_2C_2O_6 + 2e$

The structure of the potassium salt follows:

This series of salts can also be prepared by treating concentrated solutions of the carbonate or bicarbonate at --13, --16 C. with fluorine: $2Na_2CO_3 + F_2 \rightarrow Na_2C_2O_6 + 2NaF$

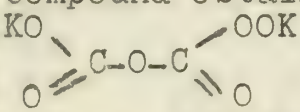
This persalt immediately liberates iodine from neutral potassium iodide solution. It is slowly hydrolyzed by ice water to the normal carbonate and hydrogen peroxide.

$$K_2C_2O_6 + H_2O \rightarrow 2KHCO_3 + H_2O_2$$

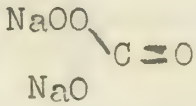
It is unstable to heat:

$$2K_2C_2O_6 \xrightarrow{\Delta} 2K_2CO_3 + 2CO_2 + O_2$$

By passing carbon dioxide into solid potassium peroxide, the compounds K_2CO_4 and $K_2C_2O_6$ were obtained by Wolffenstein and Peltner. The $K_2C_2O_6$ is not identical with the compound obtained by electrolysis and has been assigned the structure:



The structure of Na_2CO_4 has been determined as



From its synthesis by the reaction:

$$COCl_2 + 2Na_2O_2 \rightarrow Na_2CO_4 + 2NaCl + 1/2\ O_2$$

The commercial percarbonates are prepared by treating carbon dioxide with hydrated sodium peroxide. The precarbonates so formed have hydrogen peroxide of crystallization. Sodium carbonate perhydrates are made by dissolving the normal salt in hydrogen peroxide and precipitating by adding alcohol. The formula of the perhydrate is $Na_2CO_3.H_2O_2.1/2H_2O$; these are more stable than the true percarbonates.

Tin and Germanium are reported to form persalts on treating stannates and germanates respectively with hydrogen peroxide at 0°C. Jahr and Lother, however, consider the "per" germanates to be perhydrates. The so-called persilicic acid and its salts are thought by most workers to be perhydrates.

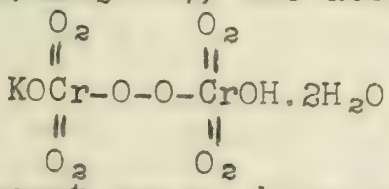
d'Ans and Friederich isolated pernitric acid, HNO_4, by dissolving nitrogen pentoxide in anhydrous hydrogen peroxide. This compound can be prepared in dilute solution by the oxidation of nitrous(but not nitric) acid with hydrogen peroxide. The pure acid is highly explosive Glau prepared a pernitrous acid solution by the action of ozone on alkali azides.

Two perphosphoric acids are known which correspond to the two persulfuric acids. The salts of both are formed when a solution of potassium hydrogen phosphate is electrolyzed in the presence of potassium fluoride. Potassium perdiphosphate, $K_4P_2O_8$, is obtained

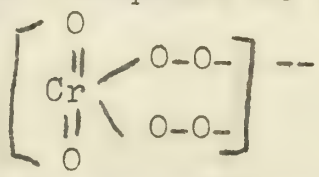
by evaporating the solution. This can be hydrolyzed to the permonophosphate in the same manner as the hydrolysis of perdisulfuric acid to Caro's acid. The permonophosphoric acid H_3PO_5 can be prepared by adding phosphorous pentoxide to 30% hydrogen peroxide. It is a very powerful oxidizing agent.

Niobium and tantalum form true peracids; the salts Na_3NbO_8 and Na_3TaO_8 are obtained by the action of an excess of an alkali metal peroxide on a solution of the sodium salt of the normal acid. Various percompounds of vanadium are known.

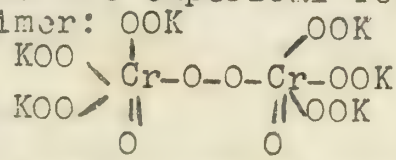
The various peracids of chromium have been extensively studied but the most generally accepted structural formulas are still not unchallenged. The blue, ether soluble, perchromates have the empirical formula, MH_2CrO_7; the accepted structure is for a dimer:



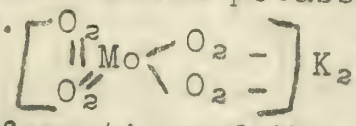
In a recent paper, however, M. E. Rumpf takes exception to this and writes the structure of the perchromate ion:



At temperatures below 0 C. hydrogen peroxide reacts with chromate solutions to give red perchromates; these have the emperical formula: M_3CrO_{16}; the structure is postulated as a dimer:



The study of the peracids of tungsten and molybdeum is complicated of isopolyperacids. These have not been characterized completely but the normal peracids are well defined. A highly unstable salt K_2MoO_8 crystallizes out when solid potassium molybdate is added to ice cold hydrogen peroxide.



The intermediate formation of this salt may be the explanation of the catalytic effect of molybdates on the decomposition of hydrogen peroxide. The corresponding pertungstates, K_2WO_8, are somewhat more stable.

The possible formation of a solution of a per perchloric acid by the action of fluorine on a perchloric acid solution was reported by Fichter and Brunner. The resulting solution had a typical peracid odor and liberated bromine from potassium bromide.

So-called perborates are a familiar article of commerce; these, however, are actually perhydrates. Some compounds have been reported as possibly being true perborates but this has never been completely established.

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Chris Best
March 18, 1941

Inorganic Chemistry--Seminar March 25, 1941

The Chemistry of Galvanizing

History: Zinc has been known since 500 B.C. Paracelsus first classified it as a metal. Commercial production was begun in Bristol, England in 1743. The first zinc coating experiments were carried out in 1741 in France. By 1778 zinc coated kitchen utensils were fairly well known in France. First a resinous flux was used, but since 1802 "sal ammoniac" has been used as flux for the process. A French patent in 1836 covers practically the whole hot dipping process as it is known today.

Terminology: The terms "galvanized" and "galvanizing" had their origin in the concept of electrochemical (galvanic) protection from corrosion. Today we do not have the same explanation for the protection given to steel by zinc coating, therefore the term galvanizing should be discarded. The American Zinc Institute advocates the use of the term "zinc coating" for any way of covering metal surfaces by zinc and the term "zinc dipping" for the hot dip process.

The Hot Dipping Process:

I. Pickling is divided into:

A) Removal of organic surface impurities by dipping into 3-7% alkali solution and subsequent electrolysis in alkali solution
B) Removal of inorganic surface impurities by the pickling liquors:
   1) Hydrochloric acid (for wires)
   2) Sulphuric acid (for sheets, stamped metal, boilers, etc.)
   3) Hydrofluoric acid (for pipes to remove iron silicate)
   4) Sodium bisulphate (for special cases)
   5) Molten salts (very rarely used)

The factors which influence the course of the pickling reaction are:

A) The acid concentration influences the solubility and the relation between the solubility of the iron and the different iron oxides
B) The solubility of steel in the pickling liquor rises with the copper content
C) The temperature has to be below 40° for hydrochloric acid and between 50 and 80°C for sulphuric acid
D) The reaction time is dependent upon the kind of oxides which are present. The time is an inverse function of temperature for hydrochloric acid, and has a minimum at 25° C if sulphuric acid is used.
E) Pickling additions are used to avoid hydrogen adsorbtion and e excess acid consumption. Basic substances of high molecular weight and concentrations up to 1 gram per liter are used. The best ones include in order of their effectiveness:
   1) Quinoline ethiodide
   2) An undefined coal tar extract
   3) Pyridine
   4) Glue

Efforts to make the old pickling process more efficient resulted in a new method, which employs active metals to replace the impurities

on the surface, and removal of these active metals by an electrolytic process using the steel as cathode in an alkali bath.

II. Fluxing: Immediately before fluxing the material passes a flux wash which is usually a weak ammonium chloride solution. This procedure is employed for the purpose of rust retardation.

A) The purpose of the flux is:

1) To dissolve all impurities still present;
2) To keep the surface free from oxides;
3) To remove the remainders of the pickling water to give a perfectly dry surface;
4) To provide a heating medium before the hot dip.

B) Fluxes in general use are:

1) Zinc chloride - ammonium chloride ($ZnCl_2.2NH_4Cl$ and $ZnCl_2.3NH_4Cl$)
2) Zinc chloride - ammonia ($ZnCl_2.5NH_3.H_2O$
3) Ammonium chloride (NH_4Cl)
4) Zinc chloride ($ZnCl_2$, used especially for protecting purposes
5) Hydrochloric acid (used especially for cleansing purposes)

C) Fluxing reactions (using ammonium chloride as flux or flux conditioner) include:

1) $Zn + 2NH_4Cl = Zn(NH_3)_2Cl_2 + H_2$
2) $Zn(NH_3)_2Cl_2 = Zn(NH_3)_2Cl_2 + NH_3$
3) $Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$
4) $FeCl_2 + Zn = ZnCl_2 + Fe$
5) $MeO + NH_4Cl = MeOHCl + NH_3$
6) $MeOHCl + ZnNH_3Cl_2 = MeCl_2 + ZnOHCl + NH_3$
7) $MeO + ZnCl_2 = ZnCl_2.MeO$

D) The fluxes contain always a certain percentage of inhibitors. The purpose of these inhibitors is:

1) To keep the flux wet in the case of dry castings and fittings which dry the flux out
2) To keep the ammonia content in the flux as stable as possible

Some of the most popular fluxes are:
1) Glycerine
2) Tallow
3) Bran
4) Sawdust

III. Hot dipping:

A) Of great importance for the understanding of the actual zinc coating reaction is the knowledge of the crystal structure of the participating metals and alloys.

B) The finished coat consists of

1) An iron zinc alloy layer which can be divided into:
   A) An unknown alloy, B) $FeZn_3$, C) $FeZn_7$
2) The zinc layer consisting of:
   A) Pure metallic zinc, B) $Zn(OH)_2$, C) $ZnCO_3$

C) Factors affecting the zinc coating reaction are:

1) The chemical constitution of the iron
2) The chemical constitution of the zinc
3) The temperature of the reaction
4) The length of the reaction

IV. Testing metals

A) Mechanical tests are used to determine the bending properties of zinc coated metal

B) Chemical tests should reveal variations in thickness of coating and enable us to compare the thickness of the coat for several specimens of the same kind. In use are:

1) The Preece test
2) The acetic acid-hydrogen peroxide immersion test
3) The sulfurous acid immersion test
4) Hydrochloric acid test
5) The Gelatine test for porosity of coatings

C) Quantitative tests determine the amount of metal used in the coating per unit area of surface covered. The most frequent ones are:

1) The hydrochloric acid-antimony chloride method
2) The Basic lead acetate method

D) Accelerated corrosion tests should obtain results within a short time which simulate those which would ultimately occur in service. They include 1) The spray test
2) The iodine test

E) Exposure tests give information as to the service life of different types of zinc coatings.

V. Protection by zinc against corrosion: The older theory said that zinc offered electrochemical protection against corrosion. Today it is agreed that zinc just excludes the iron hermetically from contact with the corrodent.

VI. Dross: Dross is pure zinc contaminated with 2-5% iron. It can be traced to four sources:

A) Destruction of the kettle itself;
B) Insufficiently cleaned metal sheets enter the kettle;
C) Iron salts in the kettle because of the use of active flux;
D) The metal sheets give off some iron;
E) Dross held in suspension

The loss in dross in an efficient plant can be reduced to 3%, but there are a number of plants in operation which have a loss of 35% zinc because of dross.

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Norman S. Landau

Tables

Table 1

World consumption of crude zinc (60% for galvanizing, 54% for hot dip)

Year	1840	1878	1895	1902	1909	1915	1920	1930	1940
100,000 tons:	.3	2.	4.	5.	8.	10.0	7.	14.0	15.

Table 2-Zinc used for hot dip galvanizing:

Used for :	Sheets	Tubes	Shapes	Wire	Wire Cloth
% of total:	54%	15%	15%	13%	3%

Table 3-Surface Impurities after Pickling (G. Schumacher):

	C	Mn	P	S	Cu	Ni	As	Fe	Acid insoluble
Sheet composition:	0.04	.32	.03	.01	.2	.8	.043..		.. %
After H_2SO_4(coat):	4.7	.27	.88	1.08	20.4	2.4	3.81	49.56	.5 %
After HCl (coat):	5.0	.28	1.44	.18	20.2	7.2	6.73	41.1	2.1 %

Table 4-Vapor pressure of ammonium chloride (H. Bablik)

Temperature (0°C):	200	260	300	340	432-438
Vapor pressure (mm Hg):	13.7	68.7	259.5	778.1	Galvanizing Temp.

Table 5-Vapor and Decomposition pressures of Zinc chloride!ammonia:

Temp.(°C)	$ZnCl_2.10NH_3$:	$ZnCl_2.6NH_3$:	$ZnCl_2.4NH_3$:	$ZnCl_2.2NH_3$:	$ZnCl_2.NH_3$
-75°	441 mm	11 mm	..	..	..
-50°	no trace	stable	..	..	..
20°	. .	300 mm	has v.p.	no v.p.	..
40°	. .	800 mm	has v.p.	no v.p.	..
50°	. .	900 mm	has v.p.	no v.p.	..
57°	. .	1600 mm	has v.p.	no v.p.	..
92°	. .	..	760°	neglble	..
216°	. .	..	..	neglble	..
271°	. .	..	..	43.6	6.7
				760 mm	has v.p.

Table 6-Change in chemical composition of flux in contact with zinc:

Heating time:	Zn%	NH_3%	Cl%	Fe%	Insoluble residue: (420°C) (H. Bablik)
Start	39.9	6.74	47.8	.22	1.1
15 minutes	41.4	5.09	47.8	.07	1.0
30 minutes	42.1	4.33	48.0	.02	1.0
45 minutes	44.5	3.65	48.1	..	1.2
60 minutes	43.0	3.22	47.2	..	1.3
90 minutes	45.3	3.53	47.1	..	1.4
120 minutes	42.3	1.93	47.7	..	..
	Similar flux containing 6% glycerine:				
Start	40.4	10.9	46.0	.8	1.2
15 minutes	38.2	8.9	45.6	.28	1.6
30 minutes	38.2	8.7	45.6	.18	1.75
45 minutes	36.3	7.7	45.2	.19	2.0
75 minutes	39.4	7.5	44.8	.11	2.1
105 minutes	39.2	6.2	44.0	.10	2.1

Table 7-Solution of mild steel in molten flux at 475°C(E.J.Daniels):

Flux:	Time t(minutes)	Loss in weight L(g/m²)	$L/\sqrt{t}$= F
$ZnCl_2$	15	26.4	7
$ZnCl_2$ and 5% NH_4Cl	15	114	29
	30	186	
	45	177	
$ZnCl_2$ and 10% NH_4Cl	15	591	150
	30	670	
	45	611-641	
$ZnCl_2$ and 16.6%NH_4Cl	7 1/2	1136	375
	15	1365	

$L = F \times \sqrt{t}$

$Sc_2(SO_4)_3$

$(NH_4)_2SO_4$

$MgSO_4$

$FeSO_4$

INORGANIC INSECTICIDES

I. Stomach Poisons

A. Arsenical Compounds.

1. Some Arsenates.

a. Lead Arsenate. $Pb_4(PbOH)(AsO_4)_3$
This insecticide may be applied as a dust by first diluting 5 to 20 parts with an inert carrier such as talc. or hydrated lime. It also may be applied as spray by suspending it in water solution (2-3 lbs. per 100 gal. of water). Its chief use is to protect deciduous fruits, gardens and truck crops, ornamental plants, and shade trees from injury by chewing insects.

b. Calcium Arsenate. $Ca_3(AsO_4)_2$ plus lime.
This compound is one third more toxic than lead arsenate and is cheaper per lethal unit. It is used on resistant insects, such as cotton boll weevils, Mexican bean beetl. and resistant plants such as forest trees.

2. Some Arsenites

a. Paris green. $Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2$.
This is a very toxic compound used mainly as a poison bait. The yearly consumption in the U. S. is about 4,000,000 pounds. The dosage for spray use is 1 lb. per 100 gal. of water. The insects controlled by it include Colorado potato bettle, canker worms, codling moths, and malarial mosquito larvae. Due to its high toxicity, it will burn the foliage of stone fruits and tender vegetables.

b. Sodium arsenites. $NaAsO_2$, Na_2HAsO_3, Na_3AsO_3.
This is also an extremely toxic compound and never used on foliages. It is used chiefly in poison baits for grasshoppers, in dips for cattle, and sometime as dust for Mormon crickets.

B. Some Fluorine Compounds.

1. Sodium Fluoride. NaF.
This compound is a contact poison as well as a stomach poiso and used chiefly as a dust for cockroaches and chicken lice. It is also used in combination with other chemicals as a wood preservative to prevent attack by termites, etc.

2. Sodium fluorosilicate. Na_2SiF_6.
The lethal dosage is about the same as for NaF and thus is used for about the same purposes. It is very effective as a poison bait for grasshoppers and Japanese beetles.

3. Dutox. $BaSiF_6$
This compound is used in sprays (4 to 6 lbs. per 100 gal. of water) or as dust (6 to 12 lbs. per acre) on resistant plants such as cotton.

4. Cryolite. Na_2AlF_6
This fluoaluminate is cheaper than the arsenates and is used chiefly in a spray (4 to 6 lbs. per 100 gal. of water) or as dust (diluted with tobacco dust or cheap flour, etc.) in conjunction with the arsenicals for codling moths, plum curculio, tobacco flea beetles.

C. Comparison of the fluorides and silicates with arsenicals.

1. Advantages of fluorides and silicates over arsenical.

a. Less toxic to higher animals and plants.

b. Cheaper and acts more rapidly

c. Acts as a stomach poison and a contact poison, as well as a repellent.

2. Advantages of arsenicals over fluorides and silicates
   a. Three to five times more toxic to insects
   b. No danger of effecting the teeth or bones of higher animals
   c. Fluorides are not compatible with Ca and Ba compounds

D. Thallous sulphates and acetates. $TlSO_4$, $TlAc_2$
These compounds are 3 to 4 times as toxic as arsenates. They are used as poison bait for ants and rats.

E. Miscellaneous stomach poisons.
   1. Borax, $Na_2B_4O_7$: larvacide for flies and mosquitoes.
   2. Tartar emetic: $KSbOC_4H_4O_6$, as spray for thrips
   3. Mercurous and mercuric chlorides: as soil poison for subterranean insects such as onion maggots and cabbage root maggots.
   4. Phosphorus: poison bait for roaches and rats.
   5. Sulphur: not important any more due to the ability of insects to develop resistance to it.

I. Fumigants

A. Hydrogen cyanide HCN
This gas is obtained by the action of acid on sodium cyanide, moisture on calcium cyanide, or purchased as the liquid in steel tanks.
Uses:
   1. It is used for the control of bed bugs, fleas, lice, rats, etc. in mills, factories, buildings of human habitation, ships, and rolling store rooms.
   2. It is also used as a fumigant for scale insects on nursery and greenhouse plants and on citrus fruits.

B. Carbon disulphide. CS_2
This fumigant is used in the soil for Japanese beetle grubs, in closed chambers for grain seeds and in houses for carpet beetles. The average dosage is 10 lbs. per 1000 cu. ft.

C. Sulphur dioxide. SO_2
Sulphur dioxide is used in dosages of 4 to 8 lbs. per 1000 cu. ft. mainly for warehouse fumigation.

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Arthur Toy
April 8, 1941

CONTROL MEASURES FOR SOME COMMON INSECTS

I. Ants.

a. Find the mound or nests of the ants in the ground and destroy it by carbon disulphide, calcium cyanide or, if there are no plants near, by equal parts of creosote and gasoline.

b. When the nests are found to be in the walls or beneath the basement floor of a house, cotton wads saturated with ethylene dichloride and carbon tetrachloride, or pyrethrum extract, should be forced into the crevices from which the ants are emerging.

c. Baits are used when the nests cannot be located. The poison baits may be put out in metal bottle caps or in short sections of soda fountain straws.

1. Thallium sulphate Bait for Sweet-loving ants.
Dissolve 2g. of thallous sulphate, carefully weighed, in 1/2 pint of lukewarm, not hot, water. In a separate container mix 1/2 pint of water, one pound of granulated sugar, 3 ounces of strained honey, and 45 cc. of glycerin. Bring this mixture to a boil and remove from the fire. Cool for about five minutes, add the solution of thallous sulphate, and stir thoroughly. Label "poison" and store in a cool plac

2. Thallium sulphate bait for protein-loving ants.

Thallous sulfate	0.5 g.
Peanut butter	75. g.
German sweet chocolate	25. g.

mix together very thoroughly.

I. Silverfish and Firebrats.

a. This insect may be controlled by liberally dusting with fresh pyrethrum powder, or sodium fluoride, about the parts of the house where they are most abundant (damp places next to the soil, about basement rooms and porches, hot places such as furnace room)

b. Silverfish may also be killed by the use of poisoned bait.

Pancake flour	200 parts by wt. or 7/8 pt.
Sodium fluoride	16 parts or about 1/4 tsp.
Powdered sugar	10 parts or about 1/2 tsp.
Powdered common salt	5 parts or about 1/4 tsp.

Mix thoroughly and scattered lightly in out-of-the-way places where it need not be swept up for a long time; or scattered among loosely crumpled paper in uncovered boxes.

II. Cockroaches:

a. The best method for control of the German roaches (small tan ones, about 1/2 inch long, most common in kitchens and bath rooms) and one which practically always give relief from other species, is to dust thoroughly all parts of the house with sodium fluoride or sodium fluosilicate. This dust should be applied in liberal quantities in the dark corners of closets, at the base of the walls in basements, under sinks, around drain pipes, behind baseboards, upon shelves, or in any cracks in the wall where the cockroaches are likely to hide. Persistent treatment will clean up the most severe infestation.

b. For American roaches (large brown ones about 1 1/2 inches long, most common in basements) and Oriental roaches (uniformly black about 1 inch long, most prevalent in damp basements and along sewer lines.) fresh pyrethrum powder, applied in the same way is very effective and not poisonous to man.

c. Tested commercial phosphorus pastes are best method for controlling the American, and the Oriental cockroaches. The paste may be spread upon cardboard and rolled into cylinders, with the

poison inside, and placed or tacked in out-of-the-way places; these are good to use when roaches are not numerous or to supplement other measures.

IV. Clothes moths and carpet beetles.

a. If infestation is widespread and intense, thorough fumigation of the entire house or of infested rooms with hydrogen cyanide or carbon disulphide is quickest method.

b. Articles not to be used for some time may best be stored in very tight trunks or boxes in the following manner: At various levels among the clothing or blankets place flakes of naphthalene or paradichloriobenzene between thin sheets of paper, using a pound of naphthalene for 20 to 100 cu. ft. On top of the clothing place a shallow pan or dish and pour carbon disulphide upon it, in a warm place away from any flame, using at least 1 lb. to 100 cu. ft. of space. Quickly close the box and seal tightly with strips of gummed paper. The carbon disulphide will destroy any stages of the insects that may be present, and the other chemical will serve as a repellent against infestation for months.

V. Bedbugs.

a. A house infested with bedbugs should be fumigated with hydrocyanic gas by an experienced operator.

b. For small localized infestation, they may be killed by spraying thoroughly all cracks and other hiding places with good Lethane or rotenone spray.

VI. Fleas.

a. A thorough treatment of the habitation of the infested animals accompanied by a dusting of the pets with dermis powder containing at least 1/2 percent rotenone, or washing with derris soaps.

b. A thorough spraying of rooms with a high grade rotenone, pyrethrum, or Lethane spray will often check an infestation in its incipiency.

c. House, or basements in which fleas are established should be fumigated with HCN gas; or by burning sulphur; or by closing the rooms tightly, one after another, and sprinkle over the floor one lb. of flake napthalene to each 100 sq. ft. The room should be tightly closed for 24 to 48 hours. Any remaining naphthalene may be swept up and enough more added to treat the next room and so on until the entire house has been treated. After such treatment, the floor should be thoroughly scrubbed with hot soap suds to kill the eggs, or use an oil mop wet in kerosene.

Arthur Toy
April 8. 1941

The Electronic Theory of Acids and Bases

I. Historical Development

From the beginning of the history of Chemistry the question as to the nature of acids and bases has been one of greatest interest. The answer has been revised many times and is at present the subject of considerable controversy.

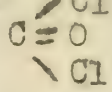
A. Four Theories
1. $H^+ + OH^-$
2. Solvent systems
3. Proton theory
4. Electronic theory

B. Other views listed Chronological order
Boyle first to define an acid
Lavoiser - O_2 necessary
* Davy - 1814 - acidity dependent on various substance
Liebig - easily replaceable Hydrogen
Arrhenius - theory of ionization

$$\text{Acid} \xrightarrow{\text{ionize}} H^+$$

$$\text{Base} \xrightarrow{\text{ionize}} OH^-$$

Folin and Flanders 1912 - titration of acids in non-aqueous solvents
Franklin - starts theory of Solvent System - shows similarity of NH_3 and H_2O
Germann - applies Solvent System - shows $AlCl_3$ is an acid in



Neutralization Reactions According to Theory of Solvent Systems

Solvent	Acid +	Base --->	Salt +	Solvent
H_2O	H_3O^+, Br^-	K^+ OH^-	K^+ Br^-	$2H_2O$
NH_3	NH^+_4, Br^-	K^+, NH_2^-	K^+ Br^-	$2NH_3$
C_2H_5OH	$C_2H_5OH_2^+$, Br^-	K^+, $OC_2H_5^-$	K^+ Br^-	$2C_2H_5OH$
SO_2	SO^{++}, Br_2^-	K_2^+, SO_3^{--}	$2K^+$ Br^-	$2SO_2$
$COCl_2$	$COCl^+$, $AlCl_4^-$	K^+, Cl^-	K^+ $AlCl_4^-$	$COCl_2$
$SeOCl_2$	$(SeOCl)_2^+$ $SnCl_6^=$	$2K^+$, Cl^-	$K_2^+SnCl_6^=$	$2SeOCl_2$
$SbCl_3$	Sb^{+++}, Br^-	$3K^+$, Cl^-	$3K^+$ Br^-	$SbCl_3$

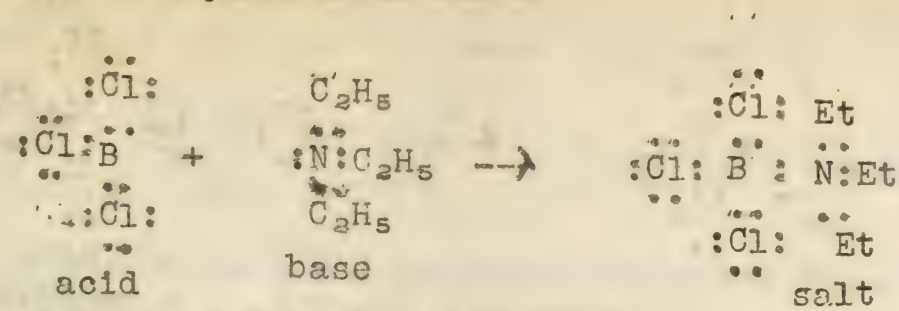
Bronsted theory - attributes acid-base properties to molecules themselves rather than to solutions.
Usonovich - emphasis on salt formation
acid gives up cations or combines with anions
base gives up anions or combines with cations

Neutralization Reactions according to Usonovich

Acid +	Base --->	Salt
SO_3	Na_2O	Na_2SO_4
Sb_2S_5	$3(NH_4)_2S$	$2(NH_4)_3SbS_4$
$Fe(CN)_3$	$3KCN$	$K_3Fe(CN)_6$
CH_3I	$(CH_3)_3N$	$(CH_3)_4NI$
Cl_2	$2Na$	$2NaCl$

Electronic Theory of Acids and Bases

Definitions based on experimental facts



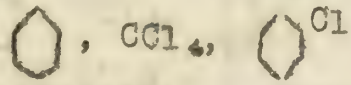
II. Role of the Solvent in Acid Basic Properties

A. Reactions of acids and bases with Solvent

1. Acid dissolves in Solvent depending on:
   (a) Strength of acid
   (b) Basic strength of Solvent

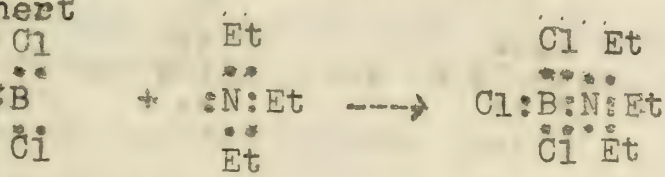
B. Neutralization and the Solvent

1. Classes of Solvents
   (a) inert toward acid and bases



   (b) Those that are ionizable
   H_2O, NH_3, SO_2, $COCl_2$, $SeOCl_2$
   (c) Those that do not ionize but react
   ROR,

2. Net result is the same for different solvents
   (a) Inert



   (b) Ionizable

$$BCl_3 + SeOCl_2 \longrightarrow SeOCl^+ + BCl_4^-$$

$$Et_3N + SeOCl_2 \longrightarrow Et_3NSeOCl^+ + Cl^-$$

$$BCl_4^-,\ SeOCl^+ + Et_3NSeOCl^+,\ Cl^- \longrightarrow Et_3NBCl_3 + 2SeOCl_2$$

   (c) Non-ionizable

$$BCl_3 + C_2H_5\ \ddot{O}:\ C_2H_5 \longrightarrow (C_2H_5)_2OBCl_3$$

$$(C_2H_5)_2OBCl_3 + (C_2H_5)_3N \longrightarrow (C_2H_5)_3NBCl_3 + (C_2H_5)_2O$$

C. Typical Reactions of Acids and Bases

1. Water solution of acid or base:
   (a) Most familiar reactions are:
      1. Free element
      2. Electrolysis
      3. Amphoteric substance

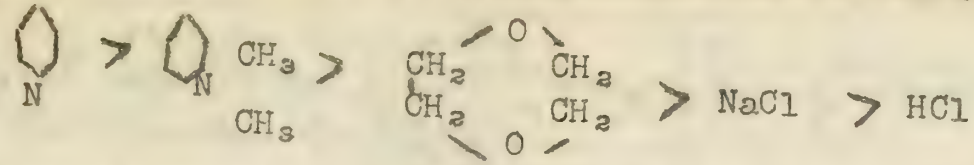
III. Further Implications of the Electronic theory of Acids and Bases

A. The extent of Acid-Base Phenomena

1. Leads to a greater degree of systematizations
2. Lewis distinguishes between:
   (a) Primary acid and bases-consideration of molecular structure reveals if molecule is an acid of base
   (b) Secondary acids and bases - molecular structure fails to reveal if the molecule is an acid or a base

B. Strengths of Acids and Bases

1. Relative strength by replacement reactions - As shown by Sisler and Audrieth's work on action of liquid NH_3 on SO_3 compounds. This arranges following compounds in decreasing basicity



2. Some reasons we have not arranged acids and bases in a sequence of strengths:

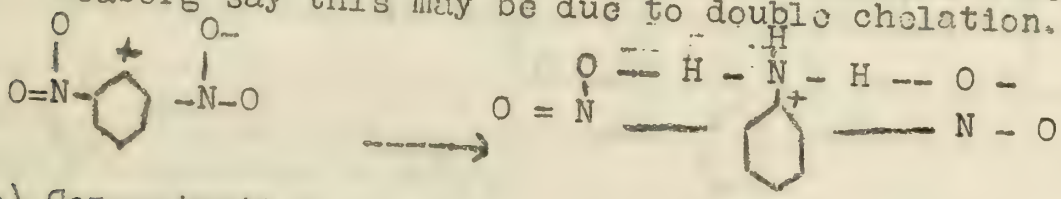
(a) "Leveling Effect"

May use inert solvent - Hantzsch finds strength of acids to be:

$$HClO_4 > HI > HBr > HCl > HNO_3$$

(b) Specific reactions cited by Lewis:

NH_3 is a weaker base than $(C_2H_5)_3N$ yet it behaves as a much stronger one toward m-dinitrobenzene - Lewis and Seaborg say this may be due to double chelation.



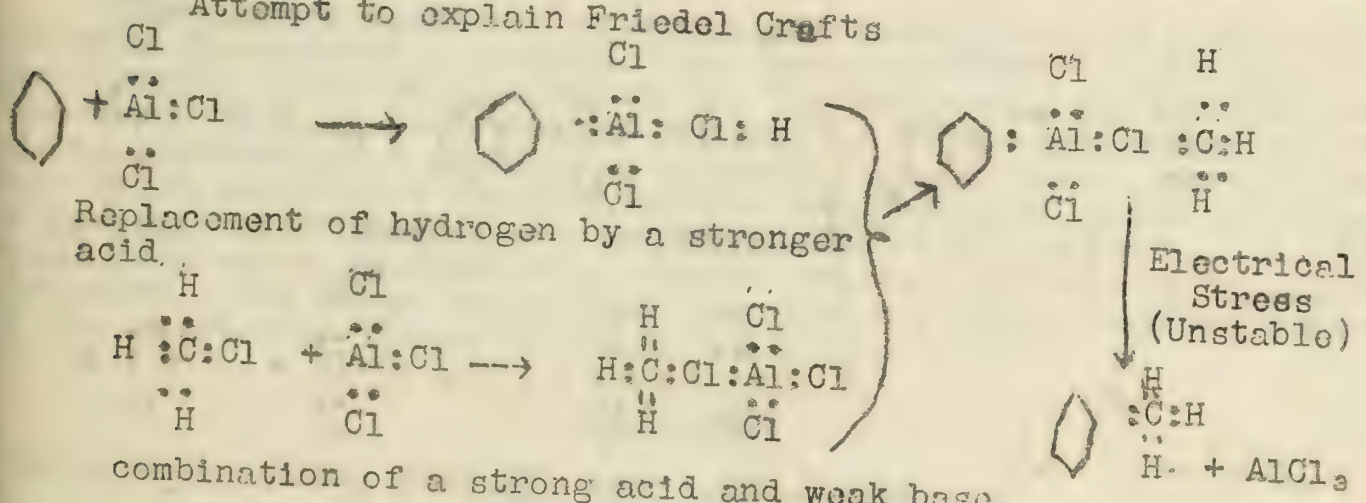
(c) Concentration

$$\underset{xs}{Zn^{++}} + NH_4OH \rightarrow \underline{Zn(OH)_2} \xrightarrow{\overset{xs}{NH_4OH}} Zn(NH_3)_4^{++}$$

C. Catalysis

Although a large amount of work remains to be done the electronic theory of acids and bases can be of great aid in a systematic interpretation

Attempt to explain Friedel Crafts



Replacement of hydrogen by a stronger acid

combination of a strong acid and weak base

D. Relationship of Acid-Base Phenomena to oxidation-reduction.

Several attempts have been made to relate these and the best results have been obtained by electronic theory of acids and bases.

Electrophilic and Electrodomic Reagents

Electrophilic Reagents: acids and oxidizing agents			Electrodomic Reagents: Bases and Reducing agents.		
Reagent	No. of Electrons Accepted		Reagent	No. of electrons donated	
	Shared, acting as an acid	Completely, ox. agt.		Shared, acting as a base	Completely red. agt.
MnO_4^-		5	Na		1
Cl_2		2	Sn^{++}		2
Fe^{+++}	6,8(1),10	1,3	SO_2	2,4	2
H_2O	2	2	H_2O	2	2
H_3O^+	2	1	CN^-	2	1
Be^{++}	4	2	S=	2,4,6,8	2
HBr	2		NH_3	2	3
BF_3	2		OH^-	2,4	2

Electrophilic - electron acceptors
Acid accepts a share in electron - Pair held by a base
Oxidizing Agent takes over completely the electrons donated by a reducing agent.
Electrodomic - electron donators
Base donates a share in an electron pair
Reducing agent loses electrons completely to an oxidizing agent

IV. Conclusions

The electronic theory of acids and bases provides a more logical and more fundamental interpretation than any other. No portion of the experimental facts is ignored by it. It is founded upon experimental behavior, with no preconceived notions as to the dependence of acidity on the presence of a particular element. It provides a general definition which attributes the distinctive properties of acids and bases to the molecules themselves, independently of the solvent. It explains these properties in terms of a simple inherent difference in electronic structure. The other two modern theories are merely limited aspects of the electronic theory of acids and bases.

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Fred Basolo
4-15-41

The Oxides of the Halogens

I. Introduction

Oxides of chlorine have been known for a long time. However, those of fluorine and bromine have only been known in the last decade. The oxides of the halogens are characterized by their great instability, which probably accounts for the reason that they have not been very carefully studied until recent years. Great precautions must be taken in their study since they will violently explode whenever they come into contact with organic material or are seriously disturbed. Many of the oxides, such as ClO_2, ClO_4, BrO_2, etc. may be considered to be free radicals that is, they contain an odd number of electrons. This may account for their great reactivity and explosiveness.

II. Chlorine oxides

A. Chlorine dioxide, ClO_2, is the most familiar of the chlorine oxides. It may be prepared by the addition of H_2SO_4 to a chlorate.

$$4HClO_3 \longrightarrow 4ClO_2 + O_2 + 2H_2O$$

or it may be prepared by heating potassium chlorate to 70° with oxalic acid when a mixture of chlorine dioxide and carbon dioxide is obtained. Electrolysis of 11.1 - 11.4 N $HClO_4$ solutions indicates that some ClO_2 is formed at the anode as well as oxygen.

1. As is true with most of the oxides of the halogens, ClO_2 is thermally unstable. However, it is more stable than most of them. It decomposes into chlorine and oxygen above the boiling point of water.

2. Chlorine dioxide is decomposed by light. A study of the photodecomposition in the presence of a small amount of water indicates that there is hypochlorous, chloric, and perchloric acids formed. Quantitative analyses for these acids lead to the postulation of the following mechanism:

$$ClO_2 + h\nu \longrightarrow ClO + O$$
$$ClO_2 + O \longrightarrow ClO_3$$
$$2ClO_3 \longrightarrow Cl_2O_6$$
$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$
$$ClO + ClO_2 \longrightarrow Cl_2O_3$$
$$Cl_2O_3 + H_2O \longrightarrow 2HClO_2 \longrightarrow HClO + HClO_3$$

Photodecomposition of the dry gas gave considerable chlorine and oxygen as well a small amount of Cl_2O_6 as indicated by the formation of a red liquid. Probably the following reaction occurs there $ClO + ClO \longrightarrow Cl_2 + O_2$.

B. Dichlorine oxide, Cl_2O, can be prepared by the addition of chlorine gas to yellow mercuric oxide.

1. Thermodecomposition of Cl_2O gives as the products, chlorine and oxygen. Below -20°C, Cl_2O is stable as is hypochlorous acid, the acid of which Cl_2O is the anhydride. Freezing point studies of a mixture of Cl_2O and water indicates an

eutectic of the composition $HOCl.2H_2O$.

2. Photodecomposition of Cl_2O produces chlorine and oxygen as the products. A proposed mechanism is as follows:

$$Cl_2O + h\nu \longrightarrow ClO + Cl$$
$$Cl + Cl_2O \longrightarrow Cl_2 + ClO$$
$$ClO + ClO \longrightarrow Cl_2 + O_2$$

C. Chlorine trioxide or dichlorine hexoxide was first observed by Millon who noticed the formation of a red liquid, when ClO_2 was exposed to sunlight. In 1925 (Z. anorg. Chem. 147, 233(1925), the oxide was prepared in a relatively pure state and analyzed. The analysis indicated that the ratio of chlorine to oxygen was 1:3. This fact, together with the value for the molecular weight as determined in CCl_4 solution, led to the formula Cl_2O_6. However Cl_2O_6 may be prepared by mixing ozone and chlorine dioxide. Because it is thermally unstable, this reaction is usually carried out at fairly low temperatures.

1. The thermal decomposition of Cl_2O_6 produces as the products chlorine and oxygen. It is fairly stable at ordinary temperatures but at slightly elevated temperatures, decomposition takes place quite rapidly.

2. Chemical properties. Cl_2O_6 has a strong affinity for water, forming chloric and perchloric acids. If added to an alkaline solution or to a solution of KI in water, there is a violent explosing which usually shatters the beaker. When in contact with grease, wood, etc., a violent explosion occurs. Solutions of Cl_2O_6 in CCl_4 are immediately decolorized by iodine, I_2O_4 and I_2O_5 being formed. Bromine doesn't appear to do this.

III. Bromine oxides

A. Bromine dioxide, BrO_2, may be prepared by electrical discharge through a mixture of bromine and oxygen at low temperatures.

1. BrO_2 is soluble in CCl_4, in petroleum ether, and in cold water with decomposition. A solution in liquid ammonia yields NH_4Br and NH_4BrO_3; in 5N NaOH solution NaBr and $NaBrO_3$ are obtained.

2. BrO_2 is thermally decomposed into other oxides, bromine, and oxygen. It is completely stable at -40°C. At -35°C, decomposition may be detected monometrically. From -3 to 18°C, bromine vapor is visible but spontaneous decomposition does not occur.

B. Bromine monoxide, Br_2O, is prepared in the thermal decomposition of BrO_2 or by the action of bromine on mercuric oxide.

1. Br_2O is soluble in CCl_4 as the monomer with some decomposition (some $COCl_2$ is formed). The solution in water is hypobromous acid showing Br_2O to be the anhydride of the acid. Solution in NaOH gives some $NaBrO_3$. Br_2O sublimes with extensive decomposition in dry air at -17.5 ± 0.5°C.

2. Br_2O is stable at temperatures up to -40°C. At 0°C the decomposition is slow.

IV. Iodine oxides

A. I_2O_5 can be prepared by the action of hot concentrated H_2SO_4 on HIO_3 or by the action of very concentrated HNO_3 on iodine. If the nitrogen oxides are removed as they are formed, in the latter reaction, I_2O_4 can be formed.

B. Iodine oxides form several complex compounds. With sulfuric acid, $I_2O_3.H_2SO_4$ and some $I_2O_4.H_2SO_4$ are produced.

$$2I_2 + 3I_2O_5 + 5H_2SO_4 \longrightarrow 5I_2O_3.H_2SO_4$$

Compounds of the type $I_2O_5.XHF$ have been formed but they have proved to be very unstable.

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O. F. Hill
April 22, 1941

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1941-1942

COLLISION THEORY AND THE KINETICS OF THE REACTION BETWEEN NITROGEN PENTOXIDE AND NITRIC OXIDE.

J. Harold Smith October 7, 1941

I. The thermal decomposition of nitrogen pentoxide.

As recently as 1925 the thermal decomposition of N_2O_5 was the only known example of a first order gas phase reaction. Over a very wide range from a few hundredths of a millimeter pressure up to 1000 mm. the specific decomposition rate has been shown to be entirely independent of the pressure and thus strictly a first order reaction.

A commonly accepted mechanism to account for the first order nature of the reaction is as follows:

1. $N_2O_5 \longrightarrow N_2O_3 + O_2$ (slow)
2. $N_2O_3 \longrightarrow NO_2 + NO$ (fast)
3. $N_2O_5 + NO \longrightarrow 3NO_2$ (fast)

$2N_2O_5 \longrightarrow 4NO_2 + O_2$ (first order)

II. Discussion of the collisional theory of first order reactions.

If the half-life period for a first order reaction were entirely independent of concentration, it should be possible to expand the gas to infinite volume without influencing the number of molecules which react in unit time. Isolated molecules unable to gain energy of activation by collision, would then have to acquire energy for activation in some other manner. Inability to account for the origin of the activational energy in any manner other than by collisions has forced the theory to assume that a "time lag" may exist between the time at which energy sufficient for activation is acquired by collision and the moment this energy becomes sufficiently localized in some particular part (bond) of the molecule to result in a transformation. On this basis, molecules might actually receive their energy of activation by collision and still react at a rate independent of the pressure over a wide range though not to the limit of infinite dilution. At extremely low pressures the rate of collision must become insufficient to supply activation - and consequently the specific rate must decrease with the pressure.

There is experimental evidence to substantiate this point of view. A decrease in the specific decomposition rate of N_2O_5 actually occurs, but at pressures of only a few hundredths of a millimeter - when the theory would expect it at a pressure of several millimeters.

On the basis of the previously mentioned mechanism for the N_2O_5 decomposition, a possible alternative explanation has been suggested for the observed decrease in the rate. While the bimolecular reaction $N_2O_5 + NO \longrightarrow 3NO_2$ is rapid at high pressures, it is conceivable that at extremely low pressures the rate of this reaction might become slow enough to limit the rate of the decomposition.

III. The reaction between nitrogen pentoxide and nitric oxide.

The reaction between nitrogen pentoxide and nitric oxide has previously been observed only in a qualitative way, and it has been described as an extremely rapid (perhaps instantaneous) gas phase reaction. In view of the interest in this reaction in connection with the collision theory and the N_2O_5 decomposition, an apparatus was constructed for measuring its rate.

A. Experimental Method.

1. Photo-colorimeter method.

A colorimetric method was employed for following the rate of the reaction which is very rapid even at pressures of reactants of only a few millimeters. The progress of the reaction was followed by the appearance of the brown NO_2 (the only colored substance involved), the concentration of which was determined by its strong absorption bands in the visible region. Light intensities were measured using a sensitive photronic cell and a micro-ammeter for measuring the current.

2. Calibration.

The photo-cell was calibrated at 0°, 15°, and 25°C against measured amounts of NO_2 in the various reaction tubes used.

B. Experimental Results.

Measurements have been made on the rate of the N_2O_5 - NO reaction at 0°, 15°, and 25°C and at pressures ranging from a few tenths of a millimeter up to 20 mm. Under these conditions the reaction was found to go at a conveniently followed rate, with a "half-life" of the order of 10 minutes (at 0°C). The temperature dependence of the reaction is quite normal. A 10° rise in temperature somewhat more than doubles the reaction rate. While the reaction is catalyzed by moisture, especially in a new tube, consistent results are obtainable in a tube thoroughly baked out and evacuated. That the reaction is essentially homogeneous is shown by the agreement of measurements taken in several tubes of different sizes and shapes where the surface-volume ratio is changed as much as 6 to 1.

The rate of the reaction is very nearly first order with respect to the N_2O_5 concentration. In contrast, the behavior of the rate with respect to the NO concentration is quite unusual. While nitric oxide is certainly used up in the reaction, the rate is influenced only slightly by the amount of nitric oxide present. The "order" of the nitric oxide concentration effect, which is only approximately 0.1 at a pressure of 1 mm., increases as the pressure is increased and decreases as the pressure is lowered. This indicates complexity of the reaction which is further suggested by the following observations:

1. While the reaction at 0°C appears to correspond to the stoichiometric equation, $NO + N_2O_5 \longrightarrow 3NO_2$, this is not exactly true at 25°C when one molecule of NO gives somewhat more than 3 molecules of NO_2.

2. The energy of activation changes slightly with temperature.

3. The "order" of the nitric oxide concentration effect is somewhat greater at 0° than at 25°C.

C. Conclusions.

This evidence proves the complexity of the reaction and indicates that at least 2 reactions are taking place simultaneously.

The following mechanism is suggested:

1. $2N_2O_5 + (NO) \xrightarrow{\text{catalyst}} 4NO_2 + O_2 + (NO)$

2. $2NO + O_2 \longrightarrow 2NO_2$

$$2N_2O_5 + 2NO \longrightarrow 6NO_2$$

The mechanism of the N_2O_5 decomposition should be reconsidered in the light of knowledge of the nature of the reaction with nitric oxide.

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Notes on H. M. State.

48% HI will dissolve many substances because it forms many complexes.

1. SnO_2 + 6HI ----> H_2SnI_6 + $2H_2O$
   ignited — Intense Yellow

   This yellow color is used in

2. AgX + cold $HI^{=}$ $[H\ Ag_3I_4]$ + 3HX↑ (X = Cl^-, Br^-, I^-)
   Upon dilution, AgI ppts.

3. $PbSO_4$ + HI ----> $HPbI_3$ + H_2O + H_2S↑

   $HPbI_3$ ↓ Dilution gives characteristic hexagonal plates of PbI_2.

   H_2S↑ The evolution of H_2 confirms presence of H_2S.

It also dissolves substances because of its reducing action.
$CrCl_3$ anhy., $SrSO_4$, $CaSO_4$, $BaSO_4$.

SOME ANALYTICAL USES OF COMPLEX COMPOUNDS

H. M. State October 14, 1941

A review of any of the usual qualitative schemes for cation analysis discloses numerous examples of the use of complexes, both in effecting separations and as reagents for confirmatory tests. A hasty mention will serve to recall these to mind. Less well known are some applications to anion analysis, some of which are recent innovations: $[Cupy_4]SO_4$ forms a characteristic precipitate with $S_2O_8^{=}$; $[Nipy_4](NO_3)_2$ forms precipitates with thiocyanates and selenocyanates and may be used to remove these anions from a solution to be tested for halides. $[Nien_3](NO_3)_2$ detects thiosulfate ion in the presence of several other sulfur anions. Sodium nitroprusside has long been used in the detection of sulfides.
$S^{=}, SO_4^{=}, SO_3^{=}, S_4O_6^{=}$ etc.

Hydriodic acid has recently been shown to be very useful in dissolving many difficultly soluble compounds by virtue of its reducing and complex-forming properties.

Complex compounds also find use as reagents for the microscopic identification of the alkaloids. $NH_4[Cr(NH_3)_2(SCN)_4]$, $K[Co(NH_3)_2(NO_2)_4]$, $Na_3[Co(NO_2)_6]$, and $K_2[CdI_4]$ are among the reagents employed for this purpose.

A comparatively recent development in analytical chemistry has been the study of complex compounds as precipitants, and a number of very satisfactory reagents have been discovered. The precipitates formed with these reagents are well crystallized, easily washed and dried, of high molecular weight (and hence have the advantage of low conversion factors), and occasionally are quite specific. For convenience these complex precipitates may be classified as follows:

Class 1. General formula, $[M\ Am_xX_y]$, where M represents a metal, Am, an amine (frequently pyridine) and X, an anion. Cu, Zn, Mn, Ni, Co, Cd, Hg, U are elements which form precipitates of this type. The method may also be used for the detection and determination of pyridine and of thiocyanate. The compounds are soluble in CS_2 and CCl_4, and in micro work they may be extracted by use of these reagents. The precipitates may be weighed as such after drying with alcohol and ether, or they may be ignited to oxides. Volumetric adaptations have been made for many of the methods. Separations from the alkalies, alkaline earths, Mg and Hg are possible. Altho this rather restricts the use of the methods, the precipitates still constitute excellent weighing forms for the elements after preliminary separation.

Class 2. General formula, $[M'Am_x]_a[M''X_y]_b$, where M' and M'' represent two different metals and the other symbols have their previous significance. Bi, Hg, Cu, Cd, Ag, Sb, and Ni are among the metals which may be precipitated and weighed as compounds of this class. In some cases four or five different compounds of this type have been developed for the determination of a single element. Certain of these precipitates permit excellent separations and all are characterized by low conversion factors.

Class 3. Oxime for Mg.
Dimethylglyoxime specific for Ni in basic and specifi
for Pd in faint acid.
Benzoin oxime -- specific for Cu in alkaline?
etc.

Class 4. $I_2NaCo(NO_2)_6$ can be dissolved in acid and the HNO_2 titrated with $KMnO_4$
$Na_3Co(NO_2)_6$ also used to ppt. Tl^{+++} (or is it Tl^{+}?)

$K_3[Cr(SCN)_6]$ will ppt. Bi as $Bi[Cr(SCN)_6]_3$, which separates Bi^{+++} from many other ions.

$NHg[Cr(NH_3)_2(SCN)_4]$ is highly specific for Hg^{++} and Cu^{+}. Ppt. the Hg^{++}, then reduce the Cu^{++} to Cu^{+}, and it also ppts.

Determination of Hg^{++}.
Ppt. HgS. This contains free S.
Dissolve the HgS in HI (Readily soluble)
Weigh residue of S. Difference in HgS.

In determining Cu^{++} by I^{-}, we must tie up the Fe^{+++}, which will liberate free I_2. Add F^{-}, which gives the stable complex FeF_6^{---}.

How get rid of F^{-} most eadily? Pour into excess of saturated boric acid. This gives HBF_4, which is very stable. (This won't even etch the beaker on boiling).

Class 3. Metallo-organic precipitates; inner complexes. The use of organic reagents is perhaps the most rapidly expanding field in analytical chemistry. Organic compounds which form precipitates with cations are characterized by having an acidic group and a co-ordinating group close enough together to permit the formation of a 5- or 6-membered ring with the metal. The precipitates themselves are generally very insoluble, colored, well crystallized, and sometimes quite specific, giving excellent separations. Of the many organic precipitants, only a few will be mentioned: Dimethylglyoxime for Ni and Pd; 8-hydroxyquinoline for Mg and Al; benzoinoxime for Cu and Mo.

Class 4. Miscellaneous precipitates (an inevitable but very convenient class). The precipitate, $K_2Na[Co(NO_2)_6]$, for the determination of K is well known, as is the tri-potassium compound for Co. More recent additions to this class are the compounds $Bi[Cr(SCN)_6]$, $Hg[Cr(NH_3)_2(SCN)_4]_2$, and $Cu[Cr(NH_3)_2(SCN)_4]$; these are of particular interest because of the excellent separations possible in the determinations of Bi, Hg, and Cu, respectively.

In addition to these gravimetric uses of complex compounds, many others are also known. Many of the lakes and colored compounds employed in colorimetric analysis are undoubtedly complexes, although the structures of many of them are unknown. The cyanide method for nickel is a well known example of a volumetric procedure based upon complex formation. The fluoride ion is used to form useful complexes in volumetric and electrolytic work. Flouride is conveniently "removed" from a solution by converting it to HBF_4.

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SOME PHASE RULE STUDIES OF SOLID SOLUTION FORMATION BY ISOMORPHOUS SALTS.

George S. Durham October 21, 1941

During the years from 1935 to 1940 under the direction of the late Arthur E. Hill a project was carried on at New York University of collecting reliable equilibrium data on the distribution of isomorphous salts between liquid and conjugate solid solutions. The purpose of these measurements was to relate if possible the distribution ratio of such salts between liquid and solid phases, with certain properties of the individual salts such as their aqueous solubilities. Five ternary systems consisting of water and pairs of alums and thirteen similar systems comprising water and pairs of isomorphous salts belonging to the picromerite series, were studied at 25°C.

From thermodynamical considerations and with the aid of certain assumptions which appear reasonable, the following theoretical equation can be derived.

$$\log R_{\ell} = \log K + \log R_s \left(f_1/f_2\right)_s$$

in which R_{ℓ} and R_s are equal to the mol ratio of the interchanging ions in the liquid and solid phases respectively; K is the distribution constant in terms of activities; and $\left(f_1/f_2\right)_s$ is the ratio of the activity coefficients of the two components in the solid phase. Using an empirical regularity observed for the activity coefficients of sulfates in the range of ionic strengths involved, it is possible to express K in terms of molar solubilities of the pure salts.

$$K \cong \left(\frac{S_1}{S_2}\right)^{\gamma/2b}$$

where S is the aqueous solubility (molarity) of the pure salt, γ is the total number of ions formed from one molecule of the salt and b is the total number of interchanging ions in one molecule of the salt.

In the cases of the alums, the theoretical equation expresses the observed relationships closely, provided the ratio $\left(f_1/f_2\right)_s$ be given a value of 1, which is the same as assuming that the alums form ideal solid solutions. However, for the picromerites, the distribution data fit the following empirical equation

$$\log R_{\ell} = \log K + m \log R_s$$

in which K is still the true distribution constant and m is a characteristic constant for each system, apparently related to the attraction or repulsion between the two components in the solid phase.

If it is assumed that the effect of the term $\left(\frac{f_1}{f_2}\right)_s$ is represented by the constant m, then it can be shown for the solid phase that

$$a_1 = kx_1^m$$

where a equals the activity and x equals the mol fraction of a component in the solid phase.

Since the true distribution constant appears in the empirical as well as in the theoretical equation, it is possible to compare calculated and observed values of log K for both the picromerite and alum systems. In general, good agreement is found when this is done.

It is interesting to note that the three Roozeboom types of distribution for ternary systems forming continuous solid solutions can be related to the value of the constant m in the empirical equation. When $m = 1$ the solid solution is ideal, giving Type I; when $m < 1$, there is a tendency toward incomplete series of solid solution, resulting in Type II; and with $m > 1$, a tendency toward compound formation is found, giving Type III. On this basis, the alum systems are examples of Type I and the picromerite systems of Type II.

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COMPLEX THIOCYANATES

J. B. Work November 4, 1941

Grossmann, in 1903, classified and discussed briefly 141 "double salts" which could be represented by the following type formulas: RT·MT; 2RT·MT; 3RT·MT; 5RT·2MT; RT·4MT; RT·MT_2; 2RT·MT_2; 3RT·MT_2; 4RT·MT_2; 5RT·2MT_2; 6RT·MT_2; RT·MT_3; 3RT·MT_3; 9RT·MT_3; 2RT·MT_4. (T = SCN^-; R = Na, K, NH_4, Cs, Rb; M^+ = Cu, Ag, Au, Tl; M^{++} = Ca, Sr, Mg, Zn, Cd, Hg, Pb, Mn, Co, Ni, Fe, Pd, Pt, VO, TiO, UO_2; M^{+++} = Al, Cr, Fe, Au, Bi, V; M^{++++} = Pt.) Some of these compounds would still be called double salts, for their aqueous solutions contain only the simple ions of the metals involved. Others, however, are true coordination compounds since their aqueous solutions contain thiocyanate groups firmly bound to metal ions. Further, still others of these salts are intermediate between the two extremes of stability. (1)

The coordination number of the metal is the main factor that determines how many thiocyanate groups associate with each metal ion. This is shown by the following summary of compounds reported in recent literature:

Cuprous thiocyanate will add one thiocyanate ion to form $[Cu(SCN)_2]^-$, as shown by the dialysis coefficient measurements of Brintzinger and Ratanarat. (2)

Cupric thiocyanate forms a red complex when treated with alkali thiocyanate in acetone solution; this may be evidence for $[Cu(CNS)_4]^{--}$ or $[Cu(CNS)_3]^-$. (3)

Besides a number of double salts with alkali thiocyanates, AgSCN forms such complex salts as $K[Ag(SCN)_2]$, $[Co\ en_3][Ag(SCN)_4]$, and $[Co(NH_3)_6][Ag(SCN)_3]Cl$. (4) (2)

Trivalent gold gives $K[Au(SCN)_4]$. (5)

Zinc can be coordinated to four thiocyanate groups, as in such compounds as $K_2[Zn(SCN)_4]$. (2)

Cadmium and divalent mercury form exactly analogous compounds in which four thiocyanate groups are associated with one metal ion, but $K[Hg(SCN)_3]$ has also been reported. (6)

The anion $[Al(SCN)_6]^{---}$ has been twice described. (2),(7)

Complex thiocyanates of the rare earths are similar to the compound $M_3[Sc(SCN)_6]$ mentioned by Sarkar. (8)

Titanous and titanyl salts are known with the anions $[Ti(SCN)_6]^{---}$ and $[TiO(SCN)_4]^{--}$. (7)

Apparently cerium and thorium form $[Th(SCN)_6]^{--}$, $[ThO(SCN)_6]^{----}$, $[Ce(SCN)_6]^{--}$ and $[CeO(SCN)_6]^{----}$. (2)

Vanadium forms complexes analogous to the above compounds of cerium and thorium.

Bismuth salts with the anion $[Bi(SCN)_6]^{---}$ are accepted, but $PbBi(SCN)_5$ has also been reported. (9)

A complete series of chromium compounds, from $[Cr(H_2O)_6]^{+++}$ through $[Cr(H_2O)_3(SCN)_3]$ to $[Cr(SCN)_6]^{---}$ was reported by Bjerrum. (10) On the other hand, Brintzinger claimed that the last member of this series was either $[Cr(SCN)_{12}]^{-9}$ or $[Cr_2(SCN)_{12}]^{-6}$. (2)

Trivalent molybdenum forms the expected hexa-coordinated anion, but pentavalent molybdenum gives $R_2[MoO(SCN)_5]$, while hexavalent molybdenum complexes with an undetermined number of thiocyanate groups.

Divalent manganese appears to form both a tetra- and a hexa- coordinated anion. (4)

The well-known color of ferric solutions in the presence of thiocyanates has been ascribed to $Fe(SCN)_3$, $[Fe(SCN)_6]^{---}$, and $Fe(SCN)^{++}$. Ionic migration, absorption spectra, and molecular weight experiments were used by Schlesinger to favor $[Fe(SCN)_6]^{---}$, Conductivity, oxidation-reduction potential, and colorimetric measurements led Moller, Bent and French, and Edmonds and Birnbaum to favor $Fe(SCN)^{++}$. Neither side has given ground in the debate thus far. (11), (12), (13), (14), (15).

The familiar deep blue color of cobalt salts in concentrated thiocyanate solution is probably due to an ion of the form $[Co(SCN)_4]^{--}$. (16)

Nickel salts complex with thiocyanate similarly to cobalt salts. (16).

Rhodium, Palladium, and platinum form complexes of the type $K_2[M(SCN)_4]$. Rhodium also is known in the compound $K_3[Rh(SCN)_6]$, while platinum exists in $K_2[Pt(SCN)_6]$. (17), (18), (19).

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THE STRUCTURES OF SILICATES

F. B. Schirmer, Jr. November 11, 1941

Attempts to establish the structures of the naturally occurring silicates by purely chemical methods made little progress. Such materials are difficult to obtain in a pure and reproducible state and analytical data for such complex substances give empirical formulas to which might be assigned a number of possible molecular formulas. The chemical attack is further complicated by the isomorphous replacement of one element by another in the crystal lattice. This replacement may occur with atoms of approximately the same atomic radius and with the same valence, in which case the numbers of atoms of each valency type remains unchanged. However, another type of replacement is quite common and results in the alteration of the apparent formulation of the compound. This type involves the replacement of one element by another of similar atomic radius, but having a different valence. For example, if aluminum replaces silicon in the anion SiO_4, the charge on the anion is increased by one and must be compensated by an equal increase in the cationic charge. This may be accomplished by the introduction of additional cations or by the replacement of one cation by another of higher valence.

The application of X-ray crystallographic analysis to the study of the structures of the silicate minerals, mainly by Bragg and his co-workers, has revealed certain broad principles upon which the structures of these compounds are based. The X-ray investigations have in some cases modified accepted formulas. They have also provided more precise significance for silicate formulas as representing, not the nature of the discrete molecules, but rather the atomic arrangement of the simplest possible unit out of which the whole three-dimensional pattern of the silicate crystal is built.

One of the striking characteristics of silicates as a group is the variation from compound to compound in the silicon-oxygen ratios (from SiO_4 to SiO_2). This is not due to differences in valence of the silicon atom. The latter is always tetravalent and in the silicates occupies the center of a tetrahedron of oxygen atoms. The apparently variable valence arises from the fact that these SiO_4 tetrahedra are able to combine with each other by sharing oxygen atoms. The different ways in which silicon and oxygen may be joined together serve as a basis for classifying the silicate structures. These structures are outlined below.

I. Silicates with discrete anions

A. The group $(SiO_4)^{4-}$, as in zircon, the garnets, the olivines, etc.

B. Complex silicate anions

1. The group $(Si_2O_7)^{6-}$, as in thortveitite ($Sc_2Si_2O_7$) and the melilites $[(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7]$
2. The group $(Si_3O_9)^{6-}$, as in benitoite ($BaTiSi_3O_9$).
3. The group $(Si_6O_{18})^{12-}$, as in beryl ($Be_3Al_2Si_6O_{18}$).

$$\frac{\text{Radius cation}}{\text{Radius anion}} = \text{radius ratio}$$

Polyhedron	Coordination Number	Minimum Radius Ratio
Cubo-octahedron	12	1.000
	9	.732
Cube	8	.732
Square antiprism	8	.645
	7	.592
Octahedron	6	.414
Tetrahedron	4	.225

If the radius ratio is less than that shown, figure below will form. Thus, in silicate, the radius ratio is .37. Hence silicates are tetrahedra.

$O^{=}/Al^{+++}$ ratio is .41, which is a borderline case. Hence, we can get both coordination numbers 6 and 4.

II. Silicates with extended anions

A. Chains or bands of linked SiO_4 tetrahedra

1. The group $(SiO_3)_n^{2n-}$, as in diopside (chains)
2. The group $(Si_4O_{11})_n^{4n-}$, as in asbestos (bands)

B. Sheets of linked SiO_4 tetrahedra

1. The group $(Si_2O_5)_n^{2n-}$, as in the micas

III. Three dimensional networks

A. The group $(SiO_2)_n$ as in quartz

B. The aluminosilicates

C. The clays

D. The feldspars and the zeolites

E. The ultramarines.

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THE HYDROGEN PEROXIDE THEORY OF ELECTROLYTIC OXIDATION

Fred W. Spangler November 18, 1941

I. Introduction

Electrolytic oxidation processes may be classified into two groups, those involving reactions which are thermodynamically reversible and those which are irreversible. In the first category - as for example, in the oxidation of ferrous to ferric ions - the process takes place at a definite potential almost identical with the reversible oxidation-reduction potential for the given system, with no appreciable changes due to the electrode material or the temperature. When the electrolytic process is thermodynamically irreversible, however, as in the oxidation of many organic compounds and of certain inorganic and organic anions, the phenomena are very complex and a satisfactory interpretation of the results appears difficult. It is this latter aspect of the subject about which we are concerned.

II. Origin of the Hydrogen Peroxide Theory

The anodic oxidation of sodium thiosulfate to tetrathionate can be formulated either as a purely electrical process,

$$2S_2O_3^{--} = S_4O_6^{--} + 2e$$

or as a chemical reaction brought about by active oxygen liberated at the anode by the discharge of hydroxyl or oxygen ions, thus:

$$2OH^- = H_2O + (O) + 2e \quad \text{or} \quad O^{--} = (O) + 2e$$

followed by

$$2S_2O_3^{--} + (O) + H_2O = S_4O_6^{--} + 2OH^-$$

or

$$2S_2O_3^{--} + (O) = S_4O_6^{--} + O^{--}$$

Observations of this reaction seem to indicate that it is chemical in nature. It was found that ~~mercuric cyanide~~ As_2O_3 and strychnine hydrochloride, which is a catalytic poison, inhibited the conversion of thiosulfate to tetrathionate. It is improbable that a very small amount of ~~mercuric cyanide~~ these poisons would have any effect on the reaction if it were electrical in nature. It was later found that other poisons or catalysts that influenced this electrolytic reaction were the same catalysts that had a marked influence on the decomposition of hydrogen peroxide. The assumption was made, therefore, that hydrogen peroxide is involved in anodic oxidation.

It has been known for years that the action of hydrogen peroxide on sodium thiosulfate leads to two alternative processes resulting in the formation of tetrathionate and sulfate, respectively:

$$H_2O_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2OH^-$$

and

$$4H_2O_2 + S_2O_3^{--} = 2SO_4^{--} + 2H^+ + 2H_2O$$

The former predominates in acid solution and the latter in neutral or alkaline medium. In electrolytic oxidation a small portion of sulfate is formed in addition to tetrathionate. If hydrogen peroxide is the active oxidant, then the amount should increase as the solution becomes more alkaline. Experimental results show that this is in fact

the case. Also, molybdate ions in feebly acid solutions catalyze the formation of sulfate in the oxidation of thiosulfate ions by hydrogen peroxide. It was found that the catalytic influence of molybdate ions could also be observed in the electrolytic process. The fact that the electrolytic oxidation of thiosulfate, like the oxidation by hydrogen peroxide, may be diverted to a large extent by the presence of molybdate ions, provides strong support for the view that hydrogen peroxide is the effective anodic oxidizing agent.

III. Statement and Application of the Theory

The primary postulate of the theory is that the OH radicals produced at the anode by the discharge of hydroxyl ions, which are always present in aqueous solutions, immediately combine irreversibly to form hydrogen peroxide, thus:

$$OH^- = OH + e; \quad 2OH \rightarrow H_2O_2$$

Under most conditions, hydrogen peroxide is formed, even at relatively low anode potentials, probably as a thin concentrated layer over the electrode surface. In the absence of a depolarizer capable of being oxidized, the hydrogen peroxide decomposes to give oxygen and water, but if a suitable depolarizer is present, it brings about oxidation in its own characteristic manner; this may be accompanied by oxidation due to the nascent oxygen arising from the decomposition of hydrogen peroxide and possibly by evolution of oxygen gas. The extent to which oxidation by hydrogen peroxide takes place will depend on the stability of the latter under the conditions of electrolysis, and all factors capable of affecting the decomposition of the peroxide may be expected to have some influence on the electrolytic oxidation.

The hydrogen peroxide formed at the anode can react in at least five ways:

1. It may bring about oxidation by accepting electrons from the depolarizer and being reconverted into hydroxyl ions. An example of this type of behavior is the oxidation of the thiosulfate ion.

2. It may bring about apparent reduction of highly oxidized compounds such as permanganate, chromate, and periodate ions, which react with hydrogen peroxide with the evolution of oxygen.

3. Its reaction with non-ionized organic compounds may result in the introduction of hydroxyl groups into the molecule. An example of this type of behavior is the chemical reaction between the peroxide and benzene to give phenolic derivatives.

4. The hydrogen peroxide or the active oxygen arising from its decomposition may bring about oxidation of a general nature. Oxidation of acetate (by nascent oxygen) $CH_3COOH \rightarrow CH_3COOOH \rightarrow C_2H_5OH + CO_2$

5. If no suitable depolarizer is present, oxygen gas will be evolved as a result of the decomposition of the peroxide.

Reactions 1 and 3 are favored when the conditions are such that the hydrogen peroxide formed is fairly stable. If any factor is present which catalyzes the decomposition of the hydrogen peroxide, the oxidation efficiency will be markedly decreased. On the other hand, an increase in hydrogen peroxide decomposition will increase the oxidation efficiency of reactions involving 2 and 4.

If hydrogen peroxide is produced anodically, the oxidation efficiency should be influenced by the following factors:

1. Anode material - smooth platinum, gold, and nickel are relatively poor catalysts, carbon is a moderate catalyst, and platinized platinum, manganese dioxide, lead dioxide, and gold and silver covered with oxides are good catalysts for the decomposition of hydrogen peroxide.

2. Catalysts - the presence of lead, silver, manganous, cupric, cobalt, and ferrous or ferric ions favors the decomposition of hydrogen peroxide.

3. Acidity and alkalinity - since hydrogen peroxide is more stable in acid than in alakline solution, it follows that when electrolytic oxidation is to be attributed to the peroxide, the efficiency should be highest in acid solution and should decrease as the pH of the medium increases.

4. Temperature - the rate of decomposition of hydrogen peroxide increases with rise of temperature, and hence it is to be expected that anodic oxidations brought about by the peroxide should decrease in efficiency as the temperature is raised.

5. Current density - when the hydrogen peroxide formed at the anode takes part almost wholly in one oxidation reaction, the current efficiency for oxidation should be greatest at low current densities, for at large current densities the concentration of hydrogen peroxide at the anode is high and its rate of spontaneous decomposition is considerable.

6. Depolarizer concentration - no matter what is the effective oxidant, an increase of depolarizer concentration should result in an increase of efficiency.

7. Foreign anions - in the electrolysis of salts of some organic acids the presence of inert inorganic salts tends to inhibit the main anodic reaction and leads to the formation of an alternative product.

IV. Conclusion

One of the chief difficulties of this theory is that it is not always possible to imitate anodic oxidations quantitatively using hydrogen peroxide as a chemical oxidizing agent. However, no serious objection to the anodic formation of hydrogen peroxide has been brought forward, and no alternative view has been proposed which is able to account for the observed phenomena of electrolytic oxidation.

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METALLIC BOROHYDRIDES

Orville F. Hill December 2, 1941

I. Preparation

Early in 1939 Schlesinger and his coworkers discovered that successive treatments of trimethyl aluminum with excess diborane at temperatures up to 80° gave a volatile compound of composition AlB_3H_{12}. For satisfactory preparation diborane must be present in somewhat greater quantity than that indicated by the equation

$$Al_2(CH_3)_6 + 4B_2H_6 \rightarrow 2B(CH_3)_3 + 2AlB_3H_{12}.$$

After each addition of diborane, products volatile at -95° were removed before further addition of diborane. The compound was purified by distillation at -80° and collected in a trap at -95°.

The similarity of beryllium to aluminum suggested a similar reaction for dimethyl beryllium. Actually, a compound BeB_2H_8 can be isolated and in such a way that intermediate products can be identified. As diborane is added the following products are obtained: (1) a glassy material rich in methyl groups, (2) a non-volatile, mobile liquid, (3) an unstable, easily sublimable solid of composition approximately CH_3BeBH_4, and, finally, a volatile final product BeB_2H_8 and a small amount of non-volatile $(BeBH_5)_x$.

It has long been postulated that compounds of the alkalis containing a BH_4^- ion should be capable of existence. Earlier attempts by Stock and Laudenkloss to prepare KBH_4 by reaction of hydrogen with $K_2B_2H_6$ failed. Since ethyl lithium is easy to prepare, lithium was picked as the alkali metal to study for a preparation of $LiBH_4$ by the methods used above. $LiBH_4$ proves to be a white solid of remarkable stability and non-volatility.

Physical Properties

The physical properties of aluminum borohydride are those of a non-ionic compound while those of lithium borohydride are nearer those of an ionic compound with the beryllium compound intermediate. (See Table). These properties are discussed later in their bearing to the structures of the compounds.

Table

Comparison of chemical and physical properties

	Diborane	Aluminum borohydride	Beryllium borohydride	Lithium borohydride
analytical formula	B_2H_6	AlB_3H_{12}	BeB_2H_8	$LiBH_4$
	increasing tendency to react as BH_4 derivatives →			
reaction formula	$(H_3B)_2$	$Al(BH_4)_3$	$Be(BH_4)_2$	$LiBH_4$
	← increasing tendency to react as BH_3 derivatives			
M.P., °C	-165.5	-64.5	123	275
B.P., °C	-92.5	44.5	91.3	dec. 275
vapor pressure at 0°, mm.	very high (>15,000)	119	0.5	very low ($\ll 10^{-5}$).

Chemical Properties

The aluminum and beryllium compounds explode with violence when in contact with air while the lithium compound is stable in dry air. All hydrolyze to liberate hydrogen, boric acid, and the corresponding hydroxide. They react with HCl as low as -80° according to the equation

$$2AlB_3H_{12} + 6HCl \rightarrow 6H_2 + 3B_2H_6 + Al_2Cl_6.$$

Lithium borohydride reacts with methyl alcohol according to the equation

$$LiBH_4 + 4CH_3OH \rightarrow LiB(OCH_3)_4 + 4H_2$$
$$\xrightarrow{\Delta} LiOCH_3 + B(OCH_3)_3 .$$

Addition of trimethylamine to the borohydrides forms compounds of the types $AlB_3H_{12}\cdot N(CH_3)_3$ and $BeB_2H_8\cdot N(CH_3)_3$. Excess $N(CH_3)_3$ forms $AlB_2H_9\cdot N(CH_3)_3$ and $BeBH_5\cdot N(CH_3)_3$ and borine trimethylamine, $BH_3\cdot N(CH_3)_3$. Addition of $N(CH_3)_3$ to $LiBH_4$ does not form a complex or borine trimethylamine.

AlB_3H_{12} forms a compound $AlB_3H_{12}\cdot NH_3$ with NH_3 but the reaction is not one of simple addition as evidenced by the formation of an amorphous white solid which changes to a colorless liquid and finally goes over to colorless crystals.

Discussion of Structure

Examination of the table of properties of the borohydrides shows that diborane is non-ionic in character, having a high vapor pressure, low melting point, etc., while lithium borohydride is ionic in character, having a low vapor pressure, high melting point, etc. There is a gradual transition as we go across the table from diborane to lithium borohydride. In chemical reactions, the diborane is very reactive towards air and oxygen as are the aluminum and beryllium compounds while the lithium compound is stable in dry air at room temperature. Also, the lithium compound shows no reaction at all towards trimethylamine, the beryllium and aluminum compounds as well as diborane reacting with it reversibly, the diborane reacting the most readily, indicating again that there is some gradual transition in structure of the compounds. Summarizing, lithium borohydride reacts according to the formula $Li(BH_4)$ while there is no indication of a BH_4 group or ion in diborane. The structures of the aluminum and beryllium compounds are intermediate. As evidence, although $Al(BH_4)_3$ has physical properties of a non-ionic compound, it does react in benzene solution with ethyl lithium to precipitate $LiBH_4$.

To explain these properties, we may consider $LiBH_4$ to be an ionic compound consisting of Li^+ and BH_4^- ions. It is possible that the degree of ionization of the compound may not be so high as that of a typical salt because of slight deformation of the BH_4^- ion. Then it is evident that the small and highly charged beryllium and aluminum ions would have greater deforming influence on the BH_4^- ion. Therefore, the ionic character of the beryllium compound will be decreased and that of the aluminum compound still less. This deformation would also make the BH_4^- ion susceptible to disruption explaining why BH_3 groups can be easily "extracted" from the aluminum and beryllium compounds.

Extension of the theory of Sidgwick, Pauling, and others of resonating single-electron bonds can be applied to these compounds in agreement with the experimental data.

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PREPARATION AND PROPERTIES OF BORON

Howard E. Kremers December 16, 1941

From the macroscopic standpoint, two types of elemental boron may be recognised, massive, and "amorphous" boron. Massive or crystalline boron is a hard, black massive material possessing a definite crystal structure, or having a concoidal fracture; it can generally be prepared in quite pure form. "Amorphous", or "Moissan" boron is generally prepared by a thermite reaction and usually implies a soft, dark colored powder; x-ray analysis gives lines characteristic of crystalline boron and indicates that a large part of the material is glassy, or truly amorphous boron. "Amorphous" boron has not been prepared pure, and much of the literature concerning "amorphous" boron is conflicting.

For the preparation of crystalline boron, the boron halides are generally used as the source of boron, and reduction may be effected by reducing agents such as hydrogen, or by thermal decomposition. Weintraub was the first to develop the technique of preparing pure boron by the reduction of boron trichloride with hydrogen in a high voltage alternating current arc between water cooled electrodes. Newkirk has done the latest work on the thermal decomposition of boron tribromide; decomposition occurred on electrically heated wires of iron, tungsten, tantalum, etc.

The thermite reaction between magnesium and boron trioxide gives "amorphous" boron, but impure products containing magnesium and often oxygen and nitrogen are always obtained. The method consists of igniting a mixture of powdered magnesium and boron trioxide in a suitable crucible; the resulting clinkers are digested with sulfuric acid and the insoluble boron is filtered off and dried. It was previously thought that it was impossible to obtain a product which contained no oxygen or nitrogen, but recent work at Syracuse University has shown that this is not true. If the conditions of preparation are carefully controlled, a product analyzing 87-90 per cent boron can be obtained. Purification of this boron has been attempted in a number of ways. Fusion with boron trioxide increases the boron content 1 - 2 per cent. By heating "amorphous" boron to its melting point in a mercury vapor arc, magnesium, nitrogen, and boron trioxide are removed by volatilization. Treatment of "amorphous" boron with hydrogen chloride has given the best "amorphous" boron analyzing about 96 per cent boron.

Much has been written concerning the composition of "amorphous" boron. Facts to be considered in determining the composition are (1) the method and conditions of preparation. (2) the fact that pure crystalline boron is completely soluble in nitric acid and the purest "amorphous" boron is only partially soluble in nitric acid, (3) the reaction with gaseous hydrogen chloride forms a stable substance containing boron and chlorine, and (4) x-ray analysis.

Pure boron resembles the black diamond in hardness, and like carbon has a high melting point (about 2,500°C.). Its electrical properties are perhaps most outstanding. At room temperature the specific resistance of boron is about 10^{12} that of copper, but the resistance decreases by one half for every 16 degree rise in temperature. At high temperatures it is a good conductor. Boron containing small amounts of carbon resembles carbon in electrical conductivity. Chemically, boron is rather inert at room temperature and is insoluble in acids and bases (except nitric acid and aqua regia) At glowing temperatures it combines readily with nitrogen and oxygen. Boron alloys with some metals, notably aluminum.

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PLANT DESIGN IN INORGANIC CHEMICAL INDUSTRY.

Howard L. Leventhal

January 6, 1942

A. Chemical Engineer - Is one who is skilled in design, construction, and operation of chemical plants.

B. Subdivisions of a Chemical Engineering design problem
   - I. Presentation of project
   - II. Materials, equipment and operation flow diagrams
   - III. Location of plant
   - IV. Foundation
   - V. Drainage
   - VI. Water, steam, piping, and pumping
   - VII. Selection of equipment
   - VIII. Plant layout and assembly
   - IX. Building
   - X. Preconstruction cost accounting

C. Fundamental Concepts
   - I. Material balance
     - Input = output + accumulation
   - II. Equilibrium relationships
   - III. Rate of reaction
   - IV. Gas laws
   - V. Economic balances

D. Units:

In spite of protracted discussions regarding the relative advantages of the English and metric system of units, the fact remains that practically all engineering work in the United States is done in English units.

E. Project:

Design a plant for the recovery of $FeSO_4$ contained in pickling liquors resulting from the pickling of steel in a galvanizing plant.

There is available 85,500 lb/day of waste liquor. The product recovered is the heptahydrate.

F. Laboratory and Semiworks Data

I. Composition of waste pickling liquor

$FeSO_4$ per cent	25
H_2SO_4 per cent	2

II. Gravities of solutions at critical point

Waste pickling liquor at 175°F.	1.216
Neutralized liquor at 136.5°F.	1.220
Evaporated liquor at 169.°F.	1.360
Mother liquor from centrifuge at 75°F.	1.255
Sludge from filter press at 136.5°F.	1.750

III. Temperature at critical points

Pickling solution at	175°F.
Liquor from second evaporator	169°F.
Liquor from crystallizer	75°F.
Mother liquor from centrifuge	75°F.
Cooling water	38°F.
Room temperature	60°F.

IV. Solubility and other data

$FeSO_4 \cdot 7H_2O$ at 75°F.	73.8 gms/100 g. H_2O
at 169°F.	198.5 "
Crystal yield, cooling from 169°F. to 75°F.	124.7 "

Crystals from centrifuge carry 5% H_2O

Crystals from drier essentially dry heptahydrate
Yield of heptahydrate considered 100%
Analysis of scrap iron:

Silicon	0.6%
Carbon	0.5%

Time for neutralization (hrs.) 48
Heat of formation $FeSO_4$ in solution B.t.u./lb-mol 167,760
Heat of crystallization $FeSO_4 \cdot 7H_2O$ " " 8,110
Weight of $FeSO_4 \cdot 7H_2O$ dry lb/ft³ 6
wet centrifuged lb/ft³ 7

V. Steam conditions

At 15 p.s.i. gage, 249°F latent heat of vaporization $\frac{\text{B.t.u.}}{\text{lb}}$ 945.3

At 2 p.s.i. gage, 218.4°F latent heat of vaporization $\frac{\text{B.t.u.}}{\text{lb}}$ 966.2

At 18 in vacuum, 169°F latent heat of vaporization $\frac{\text{B.t.u.}}{\text{lb}}$ 996.

VI. Heat transfer coefficients

Film coefficient, inside tube 6f.p.s.	B.t.u/hrxFt²x°F	805.4
outside tubes1f.p.s	" "	126.
Coefficient for cast iron		36
for copper		238
Overall coefficient, open tank, natural convection		25
evaporator		300
forced convection inside pipes		200
Sp. ht. of solution		1.0

G. Reaction Calculation

I. Weight Composition

$W \times P = w$

W = Total weight (lb.)
P = Part by weight
w = Weight of constituent (lb.)

II. Iron for neutralization

$Fe + H_2SO_4 \text{ --- } FeSO_4 + H_2$

(wt. of H_2SO_4) $\frac{M.W.Fe}{M.W.H_2SO_4}$ = Wt. of Fe required

III. Wt. of $FeSO_4$ added:

(lbs. iron added) + (lbs. H_2SO_4)-(lbs. H_2 liberated) = lbs. $FeSO_4$ added.

IV. Water removal

$W_F \frac{\text{M.W. of hydrate}}{\text{M.W. of } FeSO_4} = W_H$

W_F = Total weight of $FeSO_4$ (lb)
W_H = Total weight of hydrate (lb)
W_N = Wt. of neutralized liquor (lb

$W_N - W_H$ = Wt. of water to be removed (lb)

V. Weight of crystals from centrifuge

Crystals contain 5% free water - based on total weight

$\frac{\text{Weight of dry crystals}}{\text{Weight fraction of crystals}}$ = Weight of wet crystals from centrifuge (lb)

VI. Weight of water removed from drier

$W_C - W_D$ = water removed by drier (lb)

W_C = Weight of crystals from centrifuge (lb)
W_D = Weight of dry crystals (lb)

VII. Water removed by evaporator:

$W_N - W_C$ = water removed by evaporator (lb)

VIII. Mother liquor

(a) Crystals removed

Solubility at 169°F - solubility at 79°F = crystals removed

(b) Weight of mother liquor

(wt.of crystals) $\frac{\text{gm.of sol.}}{\text{gm.of ppt'd.crystals}}$ =Wt.of mother liquor (lb)

(c) $FeSO_4 \cdot 7H_2O$ in mother liquor

(wt.of mother liquor(lb)) $\frac{\text{gms.of crystal}}{\text{gm.of mother liquor}}$ = $FeSO_4 \cdot 7H_2O$ in mother liquor(lb)

IX. Centrifuge Mass

(a) (weight of H_2O on crystals) $\frac{\text{gm crystal}}{\text{gm } H_2O}$ = crystals dissolved (lb)

(b) Weight of dry crystals recovered

$W_D - W_S$ = wt. of dry crystals recovered (lb)

W_S = dissolved crystals (lb)

Proposed Equipment Flow Sheet

This portion of plant design involves considerations of:

(a) Available space
(b) Preferred operation sequence
(c) Piping distance

Material Balance

An unquestionable check on materials involved and products produced.

The law of material balance is: Input = Output + accumulation

Note: The above calculations necessarily precede any detail work on equipment specifications.

Reservoir Calculation:

I. Specifications

a) Storage for 3 days supply of pickling liquor
b) Storage for 1 day of mother liquor
c) Circular tank
d) Diameter of tank equal to depth
e) Tank to protrude only 1' above floor
f) Use acid brick lining
g) Back with common brick
h) Use 10% safety factor

Volume $= \frac{\pi d^2 h}{4}$ d = diameter of tank ft.
h = height of tank ft.

$= \frac{\pi d^3}{4}$

Excavation $= \pi (d-1) r^2$ r = radium of tank ft.

II. Number of bricks required

Specifications

a) 2" x 4" x 8" " = inches
b) Thickness of lining 1/3 foot
c) Allow 2% breakage

Sides require $= \frac{\text{Volume of brick up } (ft^3)}{\text{Volume brick}} =$

$= \frac{2\pi rth}{v_b}$

r = radius of tank (ft)
t = thickness of lining(ft)
h = height of lining (ft)
v_b = volume/brick ft^3

Bottom requires $= \frac{\pi r^2 t}{v_b}$

III. Heat losses

a) Temperature of mixture

$$\frac{M_{P.L.}T_{P.L.} + M_{M.L.}T_{M.L.}}{(M_{M.L.} + M_{P.L.})} = T_{MIX}$$

M = Mass lb
T = Temperature °F
M.L. = Mother liquor
P.L. = Pickling liquor

b) Losses

Fouriers Law

$q = HA\Delta t$

H = Heat transfer coefficient
A = Heating surface ft^2
t = Temperature difference °F
q = Heat transfer b.t.u./hr.

c) Temperature drop of mixture

$$t_m = \frac{L}{M_T}$$

L = Heat loss b.t.u/day
M_T = Total liquor handled/day

Neutralizing tank

I. Specifications

a) Time of neutralization 48 hours
b) Filling time 12 hours
c) Emptying time 12 hours
d) Each tank holds one day's supply
e) Use six tanks
f) Allow 10% safety factor

Vol. of tank = Volume of liquor (ft^3) + Volume of Fe(ft^3) 1.1

Pick a standard size tank available on the market to avoid cost of special construction

II. Heat losses:

Computed as above

Filter Press

I. Specifications

a) Clean once a week
b) 18" press with 1" frame

II. Volume of sludge handled

$$V_s = \frac{M_s}{P}$$

$$N = \frac{V_s}{V_c}$$

V_s = Vol. of sludge/week (ft^3)
P = Density lb/ft^3
M_s = Weight of sludge/week
V_c = Volume of cake

III. Heat loss

$q = HA\Delta t$

$$H = \frac{1}{1/h_1 + L_2/K_2 + 1/h_3}$$

h = Heat transfer coefficient
K = Conductivity B.t.u/hr x ft^2 x °F/ft

Evaporator Calculations

I. Specifications

a) Use two effects to care for shutdown
b) Operate with 15 pound steam
c) Operate under 1 and 18 inches of vacuum
d) Assume equal evaporation in both effects
e) Equal temperature drop in both effects
f) No effect of hydrostatic head
g) No foaming

II. Heat required

$Q_T = Q_F + Q_E$

Q = Heat required b.t.u
T = Total
F = Required to heat feed to boiling pt. (b.t.u.)
E = Required for evaporation

III. Steam required

$$S = \frac{Q_T}{\lambda}$$

S = Steam required lb.
λ = Latent heat of condensation $\frac{b.t.u}{lb}$

IV. Heating Area

$q = HA\ t$

H = Heat transfer coefficient obtained by experience and estimation

V. Selection of Evaporator

For minimum cost select available and standard equipment

VI. Cooling water required

a) Specification

Assume 5° differential
Water available at 68°F
Use 10% safety factor

$$\text{Water required} = \frac{Q_T \times 1.1}{T_c}$$

T_c = Temperature change per lb of H_2O °F

Crystallizer

I. Specifications

a) Batch type
b) Use Two
c) Welded construction
d) Cone angle to equal 45°
e) Diameter of cylinder to equal height of cylinder
f) Use standard condenser tubes
g) Two concentric coils
h) 10% safety factor

II. Volume

$$V = \frac{\pi D^3}{4} + \frac{\pi}{3}\ \frac{D^3}{8}$$

V = Volume of tank ft^3
D = Diameter of tank ft^3

From this calculation D is determined since V is known.

III. Heat to be eliminated

$q_T = Mq_c + Wt. \times T \times Spht.$

q_T = Total heat to be removed b.t.u.
M = lb-mols of crystals
q_c = Heat of crystallization b.t.u/lb-mol

IV. Cooling water required

$W_w = q_T/q_w$

W_w = Weight of cooling water/day lb
q_w = Heat absorbed per lb of water b.t.u/lb

V. Cooling Surface required

$A = q/H\ T$

VI. Number of coils

$$N \doteq \frac{L_T}{L_C}$$

N = Number of coils
L_T = Total length of tubing required ft.
L_C = Length of coil - ft.

VII. Equipment

Obtain standard equipment if available

Centrifugal

I. Specifications

a) Use two centrifuges
b) Each machine handle 12 charges/hour
c) Operate only during two 8 hour shifts

$C_T = O\ C_H\ N_C$

C_T = Total number of charges
O = Hours of operation
C_H = Charges/hour
N_C = Number of centrifuges

II. Liquor

$$L_C = \frac{L_T}{C_T}$$

L_C = Liquor per charge ft^3
L_T = Total liquor ft^3

III. Crystals

$$P_C = \frac{P_T}{C_T \times \rho}$$

P_C = Crystals per charge - lb
P_T = Total exit crystals
ρ = Density lb/ft^3

IV. Equipment

Use standard equipment

Drier — Assume drier 60% efficient

I. Heat requirements

$Q_T = Q_F + Q_E$

II. Steam requirement

$$S = \frac{Q_T}{\lambda} \times \frac{1}{0.6}$$

Pump

I. Specifications

a) Pump 8 hours
b) Design for 150% overload
c) Sp.g. 1.22

II. Head

Head = Elevation + equivalent length of pipe and fittings (ft

III. Use standard equipment

Economic Balance:

The previous problem did not lend itself very well to illustrate an economic balance, therefore we shall turn to another situation.

Data

a) Concentrate 400,000 lb/day of 10% caustic to 35%
b) Suitable type of evaporator $6400 per effect
c) Fixed charges, amortization and interest 45% per year
d) Steam $0.40 per 1000 lb.
e) 0.85n lb water evaporated per effect (n = number of effects)
f) 300 operating days per year
g) Labor costs independent of the number of effects

Basis - One operating day

Steam cost = $M_E \times M_S \times S_C$

M_E = Water evaporated lb
M_S = Steam required lb
S_C = Cost per 1000 lb

$$= 40{,}000 \times \left[9/1 - \frac{65}{35}\right] \times \frac{1}{0.85n} \times \frac{0.40}{1000}$$

$$\text{Steam cost} = \frac{134.40}{n}$$

$$\text{Fixed charges} = \frac{(0.45)(6{,}400)(n)}{300} = 9.60n$$

n	1	2	3	4	5
Fixed Charges	9.60	19.20	28.80	38.40	48.00
Steam	134.40	67.20	44.80	33.60	26.88
	$144.00	$86.40	$73.60	$72.00	$74.88

While these calculations show that the total cost is a minimum for four effects, the total cost for three effects is so little more that, in order to reduce the investment the three effects would be installed.

Total daily costs = $9.6n + \frac{134.4}{n}$ which may be differentiated to obtain the minimum.

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ROLL CALL

Bernay

January 13, 1942

Nikitin, Compt. rend. acad. sci. URSS 29, 571 (1940).

Xe.2ϕOH was made in presence of a little H_2S (which makes H_2S.2ϕOH. This acts as a crystal nucleus.) Xe.2ϕOH has a b.p. of 4°C. (with dissociation). It is about 1/3 as stable as Xe.2H_2S.

Kr was tried also. It gives a compound which is much less stable.

Chris Best

Schumb and Holloway, J.A.C.S. 63, 2753 (1941).

The homologous series $Si_nO_{n-1}Cl_{2n+2}$

$SiCl_4$

$Cl_3SiOSiCl_3$
Cl

$Cl_3SiOSiOSiCl_3$, etc.
Cl

These are known to n = 7 (For bromide, to n = 6).
Made by passing O and Cl over Si.

$(SiOCl_2)_4$ is a solid, m.p. 77°? These are converted to esters by alcohols. The bromides don't do this.

Brasted

Pitzer and Hildebrand, J.A.C.S. 63, 2472 (1941).

Color and Bond Character.

THE POTENTIAL OF THE YTTERBIC-YTTERBOUS ION ELECTRODE

H. A. Laitinen

February 10, 1942

I. Criticism of existing data

Walters and Pearce (1) report the value -0.578 volts (vs. normal hydrogen electrode, negative charge on electrode). This value is believed to be in error for the following reasons:

A. Zinc should be capable of reducing trivalent ytterbium. The equilibrium constant for the reaction $Zn + 2Yb^{+++} \rightleftharpoons Zn^{++} + 2Yb^{++}$, calculated from the value of Walters and Pearce, and the normal potential of the zinc electrode, is of the order of 10^6. Actually, no reduction has ever been observed.

B. The data of Walters and Pearce were obtained with a platinum indicator electrode in a solution containing Yb^{+++}, Yb^{++}, KCl and acetic acid (1 M). Kolthoff and Miller (2) have shown the existence of "mixed potentials" in solutions containing two oxidation-reduction systems not in equilibrium. In the present case, it is known that ytterbous ions are unstable in solution:

$$2Yb^{++} + H_2O \longrightarrow 2Yb^{+++} + H_2 + 2OH^-$$

and the platinum electrode can therefore behave not only as an ytterbium ion electrode but also to some extent as a hydrogen electrod.

C. Polarographic data (3) on the reduction of trivalent europium and ytterbium to the corresponding divalent ion show that the half-wave potential obtained polarographically for europium agrees with the normal potential measured by McCoy (4), while a value of -1.17 volts is obtained for the half-wave potential of trivalent ytterbium.

II. Theoretical relationship between the polarographic half-wave potential and the normal potential.

A. Fundamental diffusion conditions at the dropping mercury electrode.

1. The Ilkovic equation $i_d = 0.63nFCD^{1/2}m^{2/3}t^{1/6}$ (1)

   0.63 = geometrical constant
   nF = coulombs per mole of reduction
   C = concentration of diffusing ion in bulk of solution
   D = diffusion coefficient of diffusing ion
   m = mass of mercury flowing per second
   t = time (sec.) for the formation of a mercury drop
   i_d = diffusion current

2. The Ilkovic equation applied to the rising portion of the current voltage curve. C is replaced by $(C-C^o)$ where C^o is the concentration at the electrode surface.

B. The equation of the current-voltage curve

Assuming reversible behavior, the following equation is derived

$$\pi = \pi^o + \frac{RT}{F}\ln\frac{i_d - i}{i} + \frac{RT}{F}\ln\frac{\gamma_{III}}{\gamma_{II}}\left(\frac{D_{II}}{D_{III}}\right)^{1/2} \qquad (2)$$

At the half-wave point, $i = i_d - i$ and π becomes $\pi_{1/2}$, the second term on the right hand side dropping out.

C. The effect of the activity coefficient and the diffusion coefficient.

By analogy, and reasoning from conductance and ionic size considerations it is decided that $\gamma_{III} < \gamma_{II}$ and $D_{III} < D_{II}$ Thus the two effects tend to balance each other.

D. The theoretical development leads to the conclusion that if the electrode behavior is reversible the half-wave potential should be even closer to the normal potential than if the normal potential were measured in the usual way, neglecting activity coefficients.

III. Experimental check of the reversibility of the ytterbic-ytterbous ion electrode at a dropping mercury surface.

A. Logarithmic analysis of equation (2) leads to a slope of 0.066 volt when log $(i_d - i)/i$ is plotted against the potential. The theoretical value is 2.3 RT/F or 0.059 at 25°. The reduction therefore shows an essentially reversible character.

B. To rule out possible overvoltage effects, a dropping ytterbium amalgam electrode was studied. Ytterbium enters solution anodically in two stages $Yb(Hg) \rightarrow Yb^{++} + 2e^-$, and $Yb(Hg) \rightarrow Yb^{+++} + 3e^-$. The transition between the two processes should occur at the same half-wave potential as the reduction of trivalent ytterbium to the divalent ion. Experimental results showed a logarithmic slope of 0.200 volts, and a more positive half-wave potential (-1.05) for the anodic curve. A composite anodic-cathodic curve gave a value of -1.15 volts, which is considered the most probable value of the normal potential. The anodic dissolution of ytterbium was found to be less reversible than the reduction of trivalent ytterbium, hence it cannot be used in an exact way for the normal potential determination, but proves definitely that the normal potential cannot be less negative than -1.05 volts.

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ARTIFICIAL RADIOACTIVITY IN EXCHANGE REACTIONS

Fred Basolo February 17, 1942

Radioactive substances have found frequent employ in the study of numerous problems entirely unrelated to radioactivity proper. The activity of the radioelement has served as a means of measuring due to the ionizing properties of the emitted radiations. These properties permit the detection of extremely small quantities of radioactivity and offer a way of distinguishing the radioactive form of an element from its inactive isotope. When used thus, the radioactive substance has been called a radioactive indicator. This sensitivity to detection, and the ease with which certain atoms in an isotopic or isomorphic mixture may be recognized constitute the basis of the many applications already found for radio-elements.

I. Artificial Radioactivity
   A. Discovery:
      Artificial radioactivity was discovered by Curie and Joliot early in 1934.
   B. Certain Limitations:
      1. The half-life period must be suitably long for convenient manipulation
      2. The isotope must be easily obtained
   C. Types of Reactions and Methods of Production:
      1. Neutron reactions
         a. The simple, radiative capture, known as the n,γ reaction
         b. Neutron capture followed by proton emission, or the n, p reaction
         c. Neutron capture with alpha - particle emission, or the n,α reaction
         d. Neutron capture followed by the emission of two neutrons, or the n, 2n reaction
      2. Deuteron Reactions
         a. d, p; b. d, n; c. d,α
      3. Alpha - Particle Reactions
         a. α, n; b. α,p; c. α, 2n
      4. Proton Reactions
         a. p, n; b. p,γ ; c. p,α

Artificial Radioactive Indicators

Radioelement	Half-life	Nuclear transformations
Carbon	21 min.	${}_5B^{10}$ (d; n) ${}_6C^{11}$
Sodium	14.8 hrs.	Na^{23} (d;p) Na^{24}
Phosphorus	15 days	${}_{16}S^{32}$ (n;p) ${}_{15}P^{32}$ P^{31} (d;p) P^{32}
Sulfur	80 days	${}_{17}Cl^{35}$ (n;p) ${}_{16}S^{35}$ S^{34} (d;p) S^{35}

Artificial Radioactive Indicators

Radioelement	Half-life	Nuclear transformations
Chlorine	35 min.	Cl^{37} (d;p) Cl^{38} Cl^{37}((n;γ) Cl^{38}
Manganese	2.5 hrs.	Mn^{55} (d;p) Mn^{56}
Arsenic	27 hrs.	As^{75} (n;γ) As^{76}
Bromine	4.5 hrs.	Br^{79} (n;γ) Br^{80} Br^{81} (n;γ) Br^{82}
Iodine	25 hrs	I^{127} (n;γ) I^{128}

D. Methods of Chemical Identification and Concentration
   1. Electrochemical (Gas phase or liquid phase)
   2. Chemical
   3. Extraction - by solvents or adsorbents

E. Methods for detection of radiations:
   1. Electroscope
   2. Geiger-Muller counter
   3. Integrating ionization chamber

II. Exchange Reactions

A. Early work with natural radioactive indicators:
   1. Proved BiH_3 a stable compound by using Th_C
   2. Th_B used to study exchange in Pb compounds

B. Reactions involving halogens:
   1. Br_2 - Br^- exchange
      a. Von Gross and Agruss: They prepared a $Na\overset{*}{Br}$ solution and added liquid Br_2 to part of it, keeping the rest as a control. Both solutions were evaporated to dryness and the activities of the residues compared. They postulated the following mechanism

$$Na\overset{*}{Br} \rightleftharpoons Na^+ + {}^*Br^-$$

$$Br_2 + H_2O \rightleftharpoons Br^- + H^+ + HBrO$$

and calculated that for complete exchange, only 25% of the original activity of $^*Br^-$ should be left after evaporation of the Br_2. Actually 40% of the $^*Br^-$ remained and this discrepancy they attributed to the fact that the rate of evaporation of Br_2 was greater than the rate of hydrolysis

      b. Roginsky and Gopstein said the exchange takes place through a complex Br_3^-. $Na\overset{*}{Br} + Br_2 \rightleftharpoons Na\overset{*}{Br}_3$

$$Na\overset{*}{Br}_3 \rightleftharpoons Na^+ + Br^- + {}^*Br_2$$

They noticed that always the ratio of activity was equal to the ratio of the mass of Br_2 in the free state to that in the salt. This ease with which complete exchange could be attained they deduced as evidence for equivalence of the Br atoms.

   2. Non-equivalence of Br atoms in $CuBr_2$

Roginsky and Gopstein did this by starting with $Cu\overset{*}{Br}_2$ which they heated, $2Cu\overset{*}{Br}_2 \xrightarrow{\Delta} 2Cu\overset{*}{Br} + {}^*Br_2\uparrow$ to drive off half of the active Br. Now cooling the $Cu\overset{*}{Br}$ in presence of inactive Br_2 they obtained $Cu\overset{*}{Br}Br$ which on heatin

gave $2CuBr^{*}Br \xrightarrow{\Delta} 2Cu^{*}Br + Br_2\uparrow$. Repeating this process several times confirmed the fact that the Br atoms in $CuBr_2$ are not equally reactive.

3. $I_2 - I^-$ and $Cl_2 - Cl^-$ exchange have also been shown to occur as readily as the $Br_2 - Br^-$

C. Reactions involving manganese

Polissar has tested the following oxidation-reduction reactions:

$MnO_4^- + {}^*Mn^{++}$	No exchange
$MnO_4^- + {}^*Mn(C_2O_4)_2^-$	No exchange
$Mn^{++} + {}^*Mn(C_2O_4)_2^-$	Complete and rapid exchange
$MnO_4^- + {}^*MnO_2$	No exchange
$Mn^{++} + {}^*MnO_2$	No exchange

Of especial interest is the equilibrium between MnO_4^- and Mn^{++} which according to Launing and Yost, is established with great rapidity. The above indicates that interaction between MnO_4^- and Mn^{++} must be exceedingly slow if it occurs at all.

D. Reactions involving sulfur:

1. Anderson shows that the two atoms of sulfur in $S_2O_3^=$ are unlike by the following reactions:

$$ {}^*S + Na_2SO_3 = Na_2{}^*SSO_3$$

$$2AgNO_3 + Na_2{}^*SSO_3 = NaNO_3 + \underline{Ag_2{}^*SSO_3} + H^+ \longrightarrow {}^*S + SO_2$$

$$\underline{Ag_2{}^*SSO_3} + H_2O \xrightarrow{\text{boil}} H_2SO_4 + Ag_2{}^*S$$

The above resulted in an inactive solution whereas the $Ag_2{}^*S$ contained all the original activity.

2. Voge and Libby report evidence for the equivalence of S atoms in $(NH_4)_2Sx$.

$$(NH_4)_2S + {}^*S \xrightarrow{100^\circ} (NH_4)_2{}^*Sx$$

$$(NH_4)_2Sx + 2H^+ \longrightarrow 2NH_4^+ + H_2{}^*S\uparrow + {}^*Sx$$

In the above reactions we see that the activity is distributed between the H_2S and S, therefore indicating the equivalence of S atoms.

3. Other inorganic sulfur compounds in aqueous alkaline media show:

$S^= + {}^*SO_4^=$	36 hrs.	No reaction at 100°
$SO_3^= + {}^*SO_4^=$	36 "	" " " "
${}^*S^= + S_2O_3^=$	2 "	" " " "
${}^*S^= + S_2O_3^=$	1 day	Considerable reaction
${}^*SO_3^= + S_2O_3^=$	1 hr.	" "

E. Reactions involving Arsenic and Phosphorus:

1. Wilson and Dickinson found no exchange in ${}^*AsO_3^{\equiv} + AsO_4^{\equiv}$. They have also demonstrated that the velocity constants of opposing reactions in a reversible reaction at equilibrium are the same as when measured under conditions far from equilibrium. This was done by a study of the oxidation of $H_3{}^*AsO_3$ by I_2 in solution containing equal quantities of all components.

2. Wilson also obtained no exchange between ${}^*PO_3^{\equiv} + PO_4^{\equiv}$. This seems somewhat strange since $H_4P_2O_6 + H_2O \rightleftharpoons H_3PO_3 + H_3PO_4$.

F. Reactions involving Complexes:

1. Grinberg and Filinov demonstrated the complete exchange between ${}^*Br_2$ and the bromines in K_2PtBr_4 or K_2PtBr_6. Likewise Polessitsky got exchange between ${}^*I^-$ and K_2HgI_4.

2. Kennedy, Ruben and Seaborg studied exchange reactions of iron and obtained:

$^*Fe^{++} + Fe^{+++}$	Instantaneous exchange
$^*Fe(CN)_6^{=} + Fe(CN)_6^{\equiv}$	No "
$^*Fe^{+++} + Fe(CN)_6^{\equiv}$	" "

*Prussian Blue or *Turnbull's Blue - No exchange

3. Ettle and Johnson used $^*Cl^-$ to show that the interconversion in aqueous solution of green 1:6 $[Coen_2Cl_2]Cl$ to the violet 1:2 isomer does not proceed by an intramolecular inversion. They conclude that the inversion is due to the following equation:

$$[Coen_2Cl_2]^- \rightleftharpoons Cl + [CoenH_2OCl] \rightleftharpoons [Coen_2(H_2O)_2]^{\equiv} + Cl^-$$

4. Non-Exchange of Cobalt in certain complex salts was noted by Flagg. Exchange between Co^{++} and the Co^{+++} in the complex would be conditioned by two factors (1) The exchange reaction must be more rapid than the reduction of the Co^{+++} by H_2O. (2) The exchange $Co^{++} \rightleftharpoons Co^{+++}$ must be operative.

5. The exchange of oxalates of some complexes $[M(C_2O_4)_3]^{\equiv}$ of M^{+++}

Long made a study of the interchange of oxalates between uncombined $C_2O_4^{=}$ and complex $C_2O_4^{=}$ of Al^{+++}, Fe^{+++}, Co^{+++}, and Cr^{+++} using $^*C$. Under the given experimental conditions the $[Fe(C_2O_4)_3]^{\equiv}$ and $[Al(C_2O_4)_3]^{\equiv}$ show a rapid interchange while the other two exhibit no exchange. These results are in accordance with the assumption that the bonds in Cr^{+++} and Co^{+++} complexes are probably primarily covalent whereas those in the Fe^{+++} and Al^{+++} complexes are ionic.

III. Conclusion:

Above is mentioned only one use made of artificial radioactive elements. Besides this use in the study of inorganic exchange reactions, radioelements have been used in many other ways. Some of its other uses are: (1) study of reaction mechanisms, (2) reactions of high energy atoms, (3) behavior of material at extremely small concentrations, (4) analytical chemistry, (5) chemical properties of rare elements, (6) self-diffusion processes, (7) experiments with radioactive carbon, and (8) work in biochemistry.

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MANIPULATION OF THE PHOTOGRAPHIC IMAGE

Howard E. Kremers March 3, 1942

I. Introduction

It is frequently desirable for the photographer to change the nature of the photographic image by utilizing the chemical reactions characteristic of silver. This modification of the silver image is used for purposes of improving the photographic image or for changing the aesthetic value of the photograph.

The manipulation involves changing the character of the silver image without affecting the gelatin of the emulsion by:

A. Changing contrast.
B. Increasing or decreasing density by
   1. Deposition of metals.
   2. Deposition of compounds.
   3. Deposition of dyes.
   4. Removal of silver
C. Toning.
   1. Color of silver changed.
   2. Conversion or addition of a colored substance.
   3. Substitution of colored substances for silver.

II. The photographic negative

A. "Reduction."
   1. Without changing contrast.
      a. Farmer's reducer.
      b. Cerium sulfate.
      c. Potassium permanganate.
      d. Potassium dichromate.
      e. Quinone.
      f. Ammonium persulfate.
      g. Copper salts.
      h. Iodine.
   2. With reduction of contrast.
      a. Ammonium persulfate in very dilute sulfuric acid.
      b. Quinone.
      c. Potassium dichromate.
B. "Intensification" with
   1. Mercury salts.
   2. Quinone.
   3. Chromates.
   4. Uranium salts.
   5. Copper salts.
   6. Silver salts.
   7. Sulfides.
   8. Sodium stannite.
   9. Dyes.

III. The photographic positive.

Reduction and intensification are not generally applied to positives. The most important manipulation involves changing the color of the image ("toning").

A. Noble metals.
B. Sulfides and selenides.
C. Ferrocyanides of Cu, U, Fe, V.
D. Dithiooxamides.
E. Sodium stannite.
F. Organic dyes.
   1. Silver salts as mordants.
   2. Selective absorption in the gelatin layer.

IV. Reversal (conversion of negative to positive, and vice versa).

V. Development after fixation ("physical development").

Book by E. J. Wall "Photographic Facts & Formulas" gives a survey of this field.

DOLLAR CHEMISTRY

Howard Leventhal March 10, 1942

Essentially the mission of the Chemical Engineer is to, if necessary, lose money on a small scale, and make money on a large scale. To complete this mission detailed economic consideration is a necessity.

A. General Considerations

I. Unit Operations: heat flow, fluid flow, crushing and grinding, filtration, evaporation, distillation, drying, and crystallization.

II. Capital

a) Capital ratio: The ratio of invested capital to annual market value of production. The value of 1.63 for the chemical industry is very high in comparison with other industries.

b) Capital Law of Employment: Under prevailing conditions in a well diversified chemical manufacturing enterprise $8,500 must be invested in order to provide a job.

III. Research

a) Lines of Research: New uses for present products, new products from present materials and techniques, demands for specific products of service, latent or generally unrecognized needs, saving through improvemen of present products and processes, development of radically new technique, development of new raw material, and fundamental research

IV. Cost: The normal research expenditures, within the chemical industry, are between 2 and 3% of sales.

V. Process Development

a) Neglect to recognize economic factors in technical development work is such a common cause of failure that there is little danger of being too conservative when considering the commercial possibilities of new processes

b) Whiting's concept of process development: Beaker or laboratory stage, small-sized model, large-sized unit, semicommercial plant, and commercial plant.

VI. Project Analysis

1) Derivation of flow sheet: a) statement of reactions upon which the reaction is based

b) Description of process: A general statement of the process

c) Block form flow sheet

d) Calculation of flow sheet quantities: Selection of unit basis for calculation, application of necessary assumptions, application of experimental data, and calculation of flow sheet

e) Tabulation of flow-sheet quantities

2) Design of plant

a) Factors in choice plant capacity: Quantity of raw material available, quantity of finished product to be manufactured, and capacity of process units

b) Derivation of a multiplier for quantities in the unit flow sheets in order to transform them to plant quantities
c) Study of individual steps in process: Determination of conditions necessary to effect desired results, design of equipment, pressure losses, heat losses, material losses, and power requirements
d) Block flow sheet showing all quantities and temperatur

3) Derivation of cost estimate:
a) Investment for equipment required in each step. This should include 20% for contingencies and 10% for engineering and design
b) Investment should include working capital as follows: 1) Cash equivalent of 30 days' mill cost, 2) Accounts receivable equivalent to 30 days' sales, and 3) Inventory of finished product carried at cost
c) Summary of investment: 1) Land, including such improvements as roads, fences, railroad sidings, etc., 2) Buildings complete, and 3) Process equipment, including auxillary equipment
d) Operating costs: Ingredients, services, direct supervision, direct labor, repair labor and materials, supplies, works expense, and fixed charges
e) Determination of unit-process cost of product: This cost applies to the product as issued from the process and includes no storage, handling, packing, or other charges.
f) Determination of unit-process cost of product f.o.b. plant: Packages, packing, and loading
g) Determination of the price to yield a given return on investment. Ordinarily, a return of 20% on the full investment should be used
h) Determination of the effect of varying the cost of one or more ingredients

4) Market Survey
a) Description of product
1) Physical and chemical properties
2) Physiological action
3) Shipping classification
b) Standard specification
1) Specification of grades
2) Limits of impurities and of physical properties
3) Packing specifications
c) Consuming industries
1) Total consumption and value
2) Distribution of consumption by industries and by geographical areas
3) Distribution of consumption by important individual consumers
4) Exports
5) Possibility of developing new uses
d) Buying habits of consuming industries
1) Contracts, and basis of quotation
2) Sales methods
3) Possible substitutes and market conditions governing choice
4) Seasonal or fluctuating demand
5) Wide market or restricted to few consumers

e) Production statistics
   1) Domestic production and trend
   2) World production
   3) Imports for consumption
   4) Stock on hand
f) Competitive situation
   1) Principal competitors, their location and capacity
   2) Near-by markets
   3) Imports and dependence upon tariff
   4) Trends and possibility of new processes
g) Freight tariffs from principal producing centers
h) Comparison of manufacturing processes
   1) Raw materials: sources, reserves, availability
   2) Fuels and power
   3) Labor
   4) Capital investment
   5) Yields
   6) Costs of production
   7) Importance of by-products
   8) Health hazards
i) Probable future markets
   1) Trend of consumption
   2) Trend of prices
j) Patent situation and other legal restrictions on manufacture, sale and use

VII. Plant location
a) Source of raw material
b) Market for finished products
c) Sources of fuel and power
d) Labor supply
e) Transportation facilities
f) Relation to other industries
g) Capital requirement

VIII. Plant Design

Plant design comprises the arrangement of a) storage facilities, b) material-handling equipment, and c) process equipment in proper sequence and coordination and with regard for such other factors as future expansion, economical distribution of steam and power, etc.

B. Unit Operation Costs

I. Filter press calculations
a) Specifications: Two 24 inch presses, thirty chambers, 1 inch frames, filtering area 211 sq. ft., effective volume 8.79 ft.^{3}, slurry is a precipitated metallic salt the cake before drying is 40% moisture, dry weight 80 lb/ft^3, cake washed to 0.01% soluble matter, 8,000 gallon of slurry per 8 hour day, 300 days per year, length of cycle is two hours, daily produce 2.81 tons of solid
b) Interest
   1) Cost per ft^2 of filter area is $3.45
   2) Cost of presses
      (3.45) (211) (2) = $1,456
   3) Cost of accessory equipment will be 50% of base cost
      (1,456) (0.50) = $728

4) Total investment - $2,184
5) Daily interest at 6% per year - 300 days per year

$$\frac{2,184 \times 0.06}{300} = \$0.44$$

c) Depreciation
1) Assume 10% uniform depreciation per year
2) Daily charge

$$\frac{(2,184)\ (0.1)}{300} = \$0.73$$

d) Power cost
1) Assume power cost to be $0.01 per horse-power hour, and total consumption to be 0.005 h.p./ft²
2) Power cost per 8 hours

$$(211)\ (2)\ (0.005)\ (0.01)\ (8) = \$0.17$$

e) Cost of direct labor
1) Two men at $4 per day per man
2) Daily cost of labor = $8

f) Cost of maintenance and supplies
1) Cotton duck at $0.11 per ft², and an expected life of 22 working days at 8 hrs. per day
2) Assume filter cloth area per press equals 260 ft²
3) Cloth cost per day

$$\frac{(0.11)\ (260)\ (2)}{22} = \$2.60$$

4) Repairs - assume 3% per year

$$\frac{(2,184)\ (0.03)}{300} = \$0.22$$

5) Total maintenance $2.82 per day

g) Summary of costs

		Per cent
Interest	$0.44	3.5
Depreciation	0.73	6.0
Power	0.17	1.4
Labor	8.00	65.8
Maintenance	2.82	23.3
Daily cost	12.16	100.0

$$\text{Cost per ton of solid} = \frac{12.16}{2.81} = \$4.33$$

II. Evaporator Calculation
a) Calculation of the required initial investment presupposes a knowledge of the following engineering data
1) The types ofevaporator that are suitable, and proper materials of construction
2) The probable evaporation per square foot of heating surface under the specified operating conditions
3) The number of effects in the system

b) Estimates
1) Auxillary equipment about 30% of base cost
2) Installation and piping about 25%
3) Average life of evaporator 20 years
4) These estimates depend upon the size and operating conditions of the equipment. The above is for medium size equipment.

c) Summary of costs

		Per cent Anal.
Interest on investment	$9.23	8.0
Depreciation	7.68	6.6
Taxes and insurance	4.62	4.0
Steam	59.20	51.2
Cooling water	10.65	9.2
Labor	15.00	13.00
Maintenance	9.23	8.00
	$115.61	100.0

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Catalyst not in contact with reactants.

In separate boats.
H_2 passed over.

Na catalyst (Ni)	65% reduction
Ni close by	96% "
Ni 25 cm. away	75% "

Du Pont Patent for making the sodium.

Brit. Pat. 522, 635.

Downs Process modified.

$$\begin{matrix}\text{Na}\\ \text{Ca}\end{matrix} + \text{solid NaCl} \longrightarrow \text{Na} + CaCl_2$$

DIFFUSION IN SOLIDS

Philip S. Baker March 24, 1942

I. Introduction

A. Diffusion in solids is analogous in many respects to heat transfer in solids as far as ultimate effects are concerned. The actual mechanism is different. Gases, liquids and solids can all diffuse through solids, but it is necessary for the diffusing material to be in the fluid state. (That is, for example, in the case of the diffusion of one metal in another, the diffusion is caused by the atoms or molecules which escape from the metal by volatilization.)

B. In many cases, particularly in the class of metal hydrides, there is not actually a compound formed, but rather the solid contains a large amount of diffused gas. The gas atoms or molecules permeate the metal, flowing through the interstices

C. Capillary flow is simply one form of solid diffusion. When we think of capillarity, we usually think of the rise of a liquid or the depression of a liquid in a tube. However, the only manner in which the liquid can get from one part of the tube to another is by diffusion. We don't deny that surface attraction is the governing factor in this particular case, but it is impossible to conceive of molecules being handed along the glass surface without the aid of the kinetic energy of the diffusing substance.

D. Manner of Diffusion

1. Interstices

a. Canals or Capillaries

2. Lattice Holes

a. Movement of Lattices

II. Specific Examples

A. Diffusion through porous materials - ceramic bodies (Permeability is a term synonymous with diffusibility.)

1. Depends on several factors:

a. Material of which refractory is made
b. Physical constitution of refractory as to grain size
c. Nature of diffusing material
d. Temperature and thermal expansibility of solid
e. Thickness of specimen and pressure differential.

B. Diffusion Through Glasses and Crystals

1. In ideal crystals there is no ionic diffusion
2. In ordinary crystals:
a. Order-disorder equilibrium
b. Energy of activation
c. Diffusion anisotropy
d. Compounds which do not obey the law of definite proportions

3. Factors governing crystals and glasses are different from other substances

   a. In NaCl, diffusions are difficult except at high temperatures
   b. KCl and metal systems have channels, and diffusion occurs more readily
   c. Grain boundaries and faults occur

      1. Zeolites are important. Dehydration leaves numerous channels.

4. Measurement of diffusion

C. Diffusion of Gases in Metals

1. A selective process

   a. He diffused thru quartz, and other gases not so readily

2. Dissociation occurs first in many cases

   a. $Pd-H_2$
   b. $Cu-O_2$
   c. $Ag-O_2$

3. Alloys

   a. Types and resulting diffusion

      1. Two gas-dissolving metals
      2. One gas-dissolving metal, and one metal not dissolving the gas

D. Surface Diffusion

1. Crystal growth above melts

E. Diffusion in Organic Polymers

1. Rubber

2. Polysulfide

   a. Relation between diffusion in the polymer and the solubility of the gas in the unpolymerized substance.

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(over)

The following recent articles appeared ~~on~~ in ~~the~~ Chemical abstracts since the Seminar talk was given:

Absorption + Diffusion of Foreign Atoms into the ZnS Lattice

N. Riehl + H. Ortmann Z. physik. Chem A188, 109-26 (19:
Science Abstracts 45A, 62 (1942
C.A. 36, 4385[4] (1942)

← Self Diffusion of Zinc

P. H. Miller Jr. + F. R. Banks Phys. Rev. 61, 648-52 (
C.A. 36, 4385[6] (1942)

FLUOPHOSPHATES

Nathan E. Ballou March 31, 1942

Three fluophosphates have been prepared and studied, a large part of the investigations having been carried out by W. Lange during the period 1927 to 1933.

I. The Monofluophosphates

A. Preparation

1. P_2O_5 treated with a dilute solution of HF yields H_2PO_3F and also some HPO_2F_2 and HPF_6. The latter two are ppt'd. from solution by nitron (1), (2), (7).
2. Fusion of P_2O_5 with NH_4F at 130° forms both $(NH_4)_2PO_3F$ and $NH_4PO_2F_2$ (3), (12). They are separated by extracting the $NH_4PO_2F_2$ with alcohol.
3. K_2PO_3F is formed when concentrated KOH solution reacts with KPO_2F_2 (4), (12).

$$KPO_2F_2 + 2KOH \longrightarrow K_2PO_3F + KF + H_2O$$

Addition of a large excess of silver nitrate precipitates Ag_2PO_3F.

4. H_2PO_3F and HPO_2F_2 can be isolated by carefully hydrolyzing POF_3 in a weakly basic solution (1).

B. Compounds:

1. Ag_2PO_3F reacts with a metal chloride to give the monofluophosphate of the metal and a ppt. of AgCl. Thus, K_2PO_3F, Na_2PO_3F and $(NH_4)_2PO_3F$ have been prepared (4), (13).
2. Alkali salts are neutral to phenolphthalein but basic to methyl orange.
3. Neutral or alkaline solutions of the salts are stable to boiling water, but are readily hydrolyzed by strong acids.
4. Alkyl Monofluophosphates:

Sol in organic solvents

(a) $2CH_3I + Ag_2PO_3F \xrightarrow{50°} (CH_3)_2PO_3F + 2AgI$

$(CH_3)_2PO_3F + 2KOH \longrightarrow (CH_3)_2KPO_4 + KF + H_2O$

(b) $2C_2H_5I + Ag_2PO_3F \xrightarrow{100°} (C_2H_5)_2PO_3F + 2AgI$

(c) These compounds have a strong physiological effect

5. Monofluophosphates are similar to sulfates.

C. Equilibrium between H_2PO_3F and H_2O:

1. $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$
2. Reaction rate, k, determined by Lange and Stein (8).
3. Equilibrium constant, K, increased by addition of strong acids (11).

D. Electrolysis of a monofluophosphate solution:

1. The peroxy compounds, OPF(OH)OOH and OPF(OH)OOPF(OH)O are formed by electrolysis of aqueous solutions of sodium, potassium monofluophosphates (12).
2. In alkali OPF(OH)OOH loses oxygen and forms the monofluophosphate ion. OPF(OH)OOPF(OH)O is hydrolyzed and forms a peroxyphosphate.

II. The Difluophosphates

A. Preparation

1. The difluophosphates are formed along with the monofluophosphates as indicated under the preparation of the latter in methods 1, 2, and 4.

B. Compounds:

1. $NH_4PO_2F_2$ is obtained by adding NH_3 in CH_3OH to HPO_2F_2 (3).
2. $NH_4PO_2F_2$ gives a precipitate with strychnine, brucine, morphine, cocaine, tetramethylammonium hydroxide, and nitron.
3. In general a metal difluophosphate can be obtained by adding the metal nitrate to nitron difluophosphate. The nitron nitrate precipitates out of solution.
4. Potassium or cesium difluophosphate can be precipitated by adding to a concentrated solution of $NH_4PO_2F_2$ a potassium or cesium salt.
5. Difuluophosphates are stable but are hydrolyzed at high temperatures. Their general behavior is similar to that of perchlorates but the crystal characteristics are different (3).

III. The Hexafluophosphates

A. Preparation:

1. By allowing the solution obtained from the treatment of P_2O_5 with HF to stand 12 hours, the nitron salt of HPF_6 can be precipitated from solution (2).
2. Heating a metal fluoride with PCl_5 forms a hexafluophosphate. (7).

B. Compounds:

1. By treating nitron hexafluophosphate with a metal nitrate, nitron nitrate is precipitated and leaves the metal hexafluophosphate in solution (2)
2. Hexafluophosphoric acid is obtained by adding H_2SO_4 to $Ba(PF_6)_2$.
3. NH_4PF_6 reacts with diazonium salts.
4. The hexafluophosphate ion is decomposed only by molten alkali and boiling strong acids.

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RECENT ADVANCES IN THE ALUMINUM INDUSTRY

A. L. Oppegard April 7, 1942

I. Introduction
   A. Great development in 40 years
      7,150,000 lbs. in 1900 - 37 cents/lb.
      1,500,000,000 lbs. in U.S. in 1943 - 17 cents/lb.
   B. Many technical developments and improvements.
      1. New sources of alumina from clays, etc.
      2. High purity metal - 99.9987%
      3. Anodic oxidation - artifically produced oxide coating.

II. Methods of extracting alumina from various ores.
   A. From bauxite - $Al_2O_3 \cdot H_2O \cdot FeO$
      Usual method of leaching with NaOH.
   B. German methods
      1. From clay - the "S.T." process
         Clay: $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ plus impurities "clinkstone"
         a. Remove Al by treating with sulfurous acid.
         b. Decompose sulfite liquor into alumina and sulfurous acid.
      2. From the mineral pholonite - 20-23% Al_2O_3.
         a. Finely ground ore sintered with alkali and limestone at 1200° to form the alkali aluminate, silicic acid, and lime.
         b. Leaching with water removes the aluminate and leaves finely divided calcium silicate (used for cement)
         c. Usual process from here.
         d. Three valuable products
            Aluminum, alkali compounds, calcium silicate for cement manufacture.

III. Advances in the metallurgy of aluminum.
   A. Conventional Hall process - 99% aluminum.
   B. Refining of "crude" aluminum
      1. Hoopes' "3 layer process"
         a. Anode - bottom layer - impure Al plus Cu
         b. Middle layer - fused Al, Na, Ba fluorides
         c. Upper layer - cathode - pure Aluminum - 99.98%
      2. French refinements
         a. Anode - 67% Al, 33% Cu
         b. Electrolyte - 17% NaF, 23% AlF_3, 60% $BaCl_2$. m.p. 750°
         c. Cathode - 99.99% aluminum
      3. Swiss refinements
         a. Al lost from the anode is replaced to keep composition constant
         b. Electrolyte is a fluoride mixture known as "Chiolith" {This is a mixture of fluorides}
            m.p. - about 700°
         c. Cathode - guaranteed purity of 99.997%; have had 99.9987% {main impurities are Cu, Fe, Si}
   C. Properties of the pure metal
      1. Names
         a. England - "S.P." - spectroscopically pure
         b. France - "Raffinal".
         c. Germany - "Four Nines". - 99.99
      2. Physical properties
         a. Softer than usual metal
         b. More workable and malleable
         c. Conductivity - 65.4% that of Copper

3. Chemical properties
   a. Very resistant to corrosion; alloys more resistant; used for delicate apparatus
   b. Solubility in acid and alkali
      Rate very much slower - may take 2-3 days in 10% NaOH where ordinarily it would take 2-3 hours. Faster in NH_3
4. Uses
   Alloys, mirrors, reflectors

IV. Anodic oxidation
A. Stability of aluminum due to the resistant, tenacious oxide film on the surface. If broken, corrosion will occur. May overcome the difficulties by
   1. Using a purer metal
   2. Increasing the resisting power of the film by artificial means. This is known as anodic oxidation. It depends on the property of aluminum to form an oxide film when it is the anode in a suitable electrolyte such as sulfuric, chromic, or oxalic acid
      a. Main object - strengthen natural film with one of the same composition. Increase resistance to corrosion.
      b. Reaction believed to be due to the action of the nascent oxygen
B. Methods of application
   Choice of electrolyte depends on the use. Mirrors and reflectors require clear films
   1. Electrolytic polishing - producing bright surface.
      a. American method - Anodic treatment in HF and boric, chromic, or sulfuric acids.
      b. British Aluminum Co. Process
         Alkaline electrolyte - 15% Na_2CO_3, 5% Na_2HPO_4
   2. Anodic oxidation - alloys as well as Al
      a. General method
         Object attached to anode bar
         30-60 volts depending on electrolyte
         Run until film is as heavy as eanted
      b. Benough process -
         Chromic acid - airplane parts
      c. Alumilite process - main commercial one.
         Sulfuric acid
      d. Rapid method
         10% chromic acid at 37°
         40 volts, 0.3-0.4 amps/sq. cm.
         30 minutes.

C. Characteristics of the anodic coating
   1. Structure - amorphous
   2. Composition
      a. The oxide, not hydrated
         Less than 2% water
      b. Can boil in water and convert to the monohydrate, sealing the pores. This is the Alumilite sealing process
   3. Variation with the electrolyte
      a. Boric acid and borates
         Film forms rapidly - current soon stops
         Insoluble in electrolyte, nonadsorptive
      b. Sulfuric acid, oxalic and chromic acids
         Continues to grow with suitable potential

Soluble in electrolyte, porous
Cloudy, adsorptive

c. Transparent coatings -
20% solution of $NaHSO_4$
Used for mirrors and reflectors

4. Dimensional changes
   a. Volume of the oxide greater
   b. If the time of immersion is long and film is appreciably soluble, there will be a decrease
   c. Usually changes can be neglected.
      Greatest on screw threads
5. Efficiency of the process
   100% and over of Al removed for the current used
      Indicates some solution of the Al in acid
   Coating accounts for 60-80% of the Al

D. Uses
   1. Weather protection
      a. Sulfuric acid coating
      b. Chromic acid - Army and Navy
         Also use paint
   2. Reflectors and mirrors
   3. Efficient, high temperature electrical insulator

V. Varied uses for Aluminum
   A. Oxidized Aluminum wire used in high temperature coils

   B. Used in place of lead for cable sheaths

   C. Al alloy valves -plated with Cr to prevent "freezing"

   D. Bearing metals - Al-Zn alloy. Up to 95% Al

   E. Toothpaste tubes; cans, etc. in Germany.

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THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS

I. An Investigation of an Optical Anomaly Shown by Some Metal-Ortho-phenanthroline Complexes.

II. Spectrography as a Method of Following Reactions of Complex Compounds.

Robert C. Brasted April 21, 1942

I. It was noted in 1931 by certain investigators[1] that metal hexaquo bromcamphor-π-sulfonate - $M(H_2O)_6(BCS)_2$ - complexes of the common coordinating divalent metals underwent an anomalous behaviour when in the presence of ortho-phenanthroline. The camphor sulfonate and certain alkaloid salts such as strychnine also were affected. When a three molar portion of ortho-phenanthroline was added to the zinc bromcamphor-π-sulfonate salt the rotation of the complex due to the active BCS- was greatly exalted. With the addition of strychnine to $(Zn(phen)_3)^{++}$ an abnormal decrease in the rotation of the strychnine was noted. α-α'dipyridyl was not as effective in the anomaly and primary amines were without effect. The effect was attributed to an activation caused by the ortho-phenanthroline on coordination, forming an asymmetric configuration on the zinc complex. The present investigators felt that a more complete study of the whole phenomenon was necessary. The following points were studied:

A. Polarimetric study of the optical rotation of varying mols of the BCS^- and $(Zn(phen)_3)^{++}$ ions.
B. Refractometric study of the solutions made up for (A).
C. Conductivity studies of the pure complexes and related complexes for ionization data.
D. Ultraviolet and near ultraviolet studies on ortho-phenanthroline complexes and related complexes.

Results: The polarimetric and refractometric studies show the tendency for a compound formation in solution when a 2:1 ratio of BCS^- and $(Zn(phen)_3)^{++}$ exists. The same results are found for the strychnine compound. The conductivity measurements indicate an incomplete ionization which is contrary to the assumption of the previous investigators. The spectrographic data indicate a definite weighting effect since the maximum of ortho-phenanthroline is shifted to shorter frequencies when the complex with BCS^- is formed Generally the anion is quite ineffective as far as spectra of the complex are concerned.

Conclusions: Some type of compound has been formed between the anion and cation (or complex and alkaloid). The forces may well be of the Van derWaals type rather than ionic. The force has caused a distortion in the configuration which is responsible for the optical activity leading to a new activity. The assumption of "activation" does not fit in with the experimental data.

II. Initially a study of the reaction between sodium nitrite and the active $(Coen_2ClNH_3)Cl$ was desired. The rotation of the latter salt is found to decrease rapidly in the presence of nitrite giving finally an inactive product. The intermediate products would be exceedingly hard to isolate and the constitution thus indeterminable

especially in view of the fact that most of these intermediates do not differ markedly in color. A spectrographic method for following such reactions was devised by studying the changes in ultraviolet absorption. The modifications involved essentially the elimination of a plate calibration and the judicious use of a Leeds-Northrup Microdensitometer. This enabled one to make as many as fifteen spectrograms on one plate with an hour's time while the period of completing a study including the plots was cut by 70-80 per cent with an untold saving on eye fatigue compared to the use of the Gortner instrument. The relative curves so obtained compare very favorably with true curves found in the literature. Certain preliminary studies were carried out first on aquotizations while the emphasis on the later work was on the study of nitrite complex preparations and reactions.

A. A study was made of the aquotization of certain complex aniline derivative-diethylene diamine cobalt complexes previously prepared by L. B. Clapp[2]. These were found to be quite unstable in solution as indicated by an ever increasing transmission in the ultraviolet and the development of a maximum at the wave length typical of the chloro aquo complex.

B. The aquotization of cis and trans $(Coen_2Cl_2)Cl$ was followed spectrographically with time curves. The cis compound was found to aquate more readily as indicated by a shift of the initial maximum toward the higher frequency. The trans was more stable but finally aquated giving a product whose maximum was similar to that of the cis complex.

C. The relationship between the mol ratio of nitrite and trans $(Coen_2Cl_2)Cl$ was studied and the increment of E per mol of nitrite indicated a method of determining the number of NO_2 groups in a complex.

D. The nitrite-cis chloro ammine complex study was followed with relation to the changes in optical activity. The maximum typical of chloro nitro compounds increased in E value as the rotation decreased giving a final value at zero rotation typical of cis chloro nitro compounds. This curve is not readily distinguishable from cis dinitro since both have almost identical maxima. The maximum for the chloro ammino salt shifts immediately on the addition of nitrite although the change in rotation is very slight. It is possible that the final reaction product is a mixture of cis and trans salts since the location of the maximum is not that of pure cis chloro nitro or dinitro complexes.

E. The preparation of trans $(Coen_2ClNH_3)Cl$ entailed a multistep process[3] involving the formation of a slightly soluble chloro thiocyanato complex which is finally oxidized by perhydrol to the chloro ammine. Practically this synthesis was found to be an extremely uncertain one. Ultraviolet absorption showed that isomerization took place in the purification of $(Coen_2ClSCN)SCN$ to form $(Coen_2(SCN)_2)Cl$. Further, the crystallization of pure $(Coen_2ClNH_3)Cl$ from an alcoholic solution was never attained. The dithiocyanato complex unreacted, was the only crystalline product obtained from the reaction mixture. Fresh perhydrol was found to react explosively with the

thiocyanato complexes unless precooled to ice bath temperatures and stirred while the perhydrol is added dropwise. The preparation of the trans salt was finally accomplished by the treatment of $(Coen_2Cl_2)Cl$ (trans) with a CH_3OH-NH_3 solution and the fractional precipitation of the trans chloroamino isomer with dithionate as the last fraction.

References

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THE AQUO AMMONO PHOSPHORIC ACIDS

I. Preparation of the Phenyl Esters of Amido- and Diamidophosphoric Acids and Their N-substituted Derivatives.

Arthur Toy

April 28, 1942

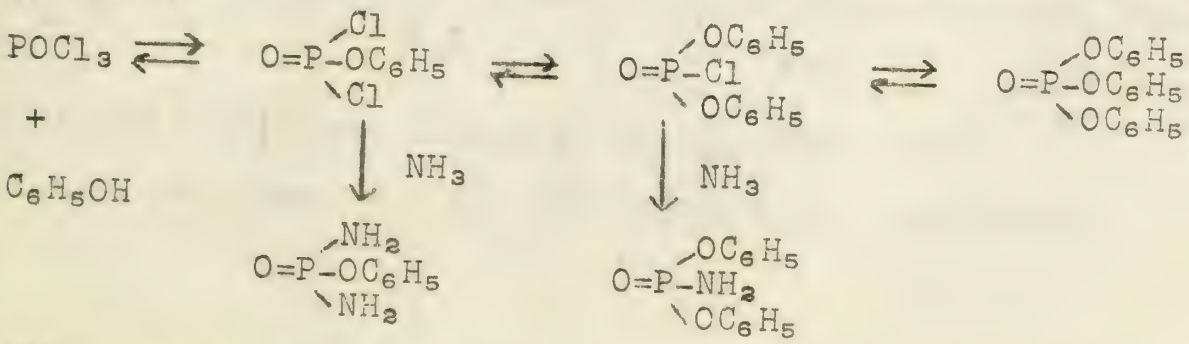
A. Introduction

In extending the studies carried out in this laboratory on the sulfamic acids, it was considered to be of distinct theoretical and technical interest to undertake an investigation of the analogous nitrogen derivatives of the phosphorus compounds, especially those which might appropriately be termed, from the Franklin (1) point of view, the phosphamic acids. The synthesis of these acids necessitated the preparation of the intermediate phenyl esters in considerable quantities. Stokes (3) had previously prepared these esters in poor yields by the treatment of the respective chlorophosphates with aqueous or alcoholic ammonia. This method was found to be unsatisfactory because the preparation of the chlorophosphates involves long heating and tedious fractionations. Therefore it seemed desirable to develop an easier and more practical method for the preparation of the phenyl esters of these aquo ammono phosphoric acids.

King and Nicholson (2) have described the synthesis of the phenylphosphoric acids by the hydrolysis of the product obtained when molar proportions of phenol dissolved in pyridine are allowed to react with phosphoryl chloride. The latter reaction takes place quickly without the necessity of prolonged heating. It was considered quite probable that ammonolysis and aminolysis of the product of interaction of phosphoryl chloride and phenol in the presence of pyridine would afford a simple method for preparing the amides as well as the N-substituted amides of the alkyl and aryl phosphoric acids. A more extended study of this procedure was therefore undertaken in order to adapt it to the preparation of phenyl diamido- and diphenyl amidophosphates and their N-substituted derivatives.

B. Discussion of the Experimental Results.

The experimental results indicate that a complex equilibrium is established when phosphoryl chloride and phenol react in the presence of pyridine.



Pyridine not only effects removal of hydrogen chloride, but also the stabilization of the intermediate chlorophosphates presumably with the formation of pyridine complexes. Rise in temperature, increase in the molar ratios both of pyridine and of phenol to phosphoryl chloride, favor a shift in the equilibrium to the right. It was found

best to use chloroform as solvent and diluent for the reaction (a) since it permitted more careful temperature control and (b) because the reaction product was found to be completely soluble in it. Ammonolysis of the resulting product may be effected by aqueous or gaseous ammonia, but liquid ammonia was found not only to be most convenient, but also to give higher yields of the products. For best results, a $POCl_3$: C_6H_5OH:C_5H_5N molar ratio of 1:0.77:3 should be used when phenyl diamido phosphate is desired, while the ratio of 1:2:3 is recommended when the diphenyl amidophosphate is desired. Though a mixture is always obtained, the two can be separated easily by hot chloroform which dissolves readily the diphenyl amidophosphate, while the diamido-phosphate is only very slightly soluble.

This method was extended to aminolytic reactions for the preparation of the N-substituted derivatives. For purposes of identification, the N-substituted derivatives were first prepared by the direct action of the phenyl chlorophosphates on the amines. The compounds prepared were the phenyl di-(methylamido)-, di-(cyclohexylamido) di-(anilido)- and di-(morpholido)-phosphates, and the diphenyl methylamido-, morpholido-, cyclohexylamido-, and anilidophosphates.

The aminolysis of the $POCl_3$-C_6H_5OH-C_5H_5N mixture as a means for preparing these compounds was found to be only partially successful, due to the fact that mixtures are always obtained. For the monophenyl N-substituted derivatives a $POCl_3$:C_6H_5OH:C_5H_5N ratio of 1:0.77:3 was employed; for the diphenyl derivatives a ratio of 1:2:3 was used. Phenyl di-(methylamido)-phosphate was obtained in good yield because it is less soluble in cold carbon tetrachloride than the by-product diphenyl methylamidophosphate. The phenyl di-(morpholido)-phosphate is soluble in water, permitting its separation from the water insoluble by-products. In case of the other compounds, suitable solvents for the separation of monophenyl derivatives from the diphenyl derivatives were not found.

This procedure is even less successful where the diphenyl N-substituted phosphates are desired. Triphenyl phosphate is always obtaine as a by-product. Substitution of amine for ammonia results in products which closely resemble the triphenyl phosohate in solubilities making separation difficult, if not impossible.

C. Bibliography

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II. N-substituted Derivatives of Phosphoryl and Thiophosphoryl Triamide as Hydrogen Bonding Agents.

A. Introduction

The esters of phosphoric acids have been used widely as plasticizers for various polymeric substances which contain active acceptor atoms. Hydrogen bonding is considered to play an important role for it is assumed that the oxygen atoms in the phosphoric acid esters serve as the donor atoms in bonding to active hydrogen atoms. Copley, Zellhoefer, and Marvel (1,2) have shown that the extraordinary solubility of CH_2Cl_2 in a series of phosphoric acid esters may be explained on the basis of the hydrogen bond theory.

The analogous N-alkyl and N-aryl substituted derivatives of phosphoryl triamide, $PO(NH_2)_3$, may be looked upon as ammono esters. Theoretically, the ammono phosphoric acid esters should serve as hydrogen bonding agents because of the presence of both oxygen and nitrogen atoms which may be capable of acting as donor atoms.

Donor molecules have been found to exhibit extraordinarily high solubility in such solvents as chloroform, which contains a labile acceptor hydrogen atom. On the other hand solubility of these same materials in solvents such as carbon tetrachloride is considerably less due to the absence of an active hydrogen atom in carbon tetrachloride. In order to determine the effect of structure upon hydrogen bonding ability, a series of N-substituted phosphoryl and thiophosphoryl triamides were prepared and these together with related compounds were investigated for their solubility in chloroform and in carbon tetrachloride at 25°.

B. Discussion of the Experimental Results

The preparation of the N-substituted phosphoryl triamides was simplified and improved by making use of a solution of the phosphoryl chloride-pyridine complex in chloroform. Aminolysis of this product was found to proceed smoothly and to give the desired compound in better yields than any method heretofore suggested.

The marked differences in solubility of the N-substituted phosphoryl triamides in chloroform and in carbon tetrachloride is especially striking in the case of the morpholine derivatives in which oxygen atoms are located in peripheral positions in the ring and the nitrogen atoms are devoid of hydrogen. The derivatives of aniline and amines of similar structures are more soluble in chloroform than in carbon tetrachloride, but the solubility in chloroform is very low in every case. This may be due to the fact that the nitrogen atom is attached in each case directly to a phenyl ring which permits the pair of free electrons on the nitrogen to resonate with the electrons in the double bonds of the phenyl ring. Thus the availability of nitrogen as a donor atom is decreased. This hypothesis is substantiated by the observation that elimination of resonance (a) by reduction of the ring, as in the case of the cyclohexylamine derivative, or (b) by separating the nitrogen from the phenyl group by means of a CH_2 group, as in case of the benzylamine derivative, brings about a great increase in solubility in chloroform. The p-phenetidine derivative, with an ether oxygen atom attached to the ring, is more soluble

in chloroform than the anilide. Presumably the extra oxygen atom serves as another donor atom, but this increase is not of the same order of magnitude as that observed in the morpholine derivatives where the oxygen atom is in the ring. The difference may be due to the fact that the electrons in the oxygen next to the phenyl ring are in resonance with the electrons in the double bonds in the ring.

Much lower solubility in chloroform is observed in the compounds where the oxygen atom, connected directly to the phosphorus atom, is replaced by a sulfur atom which is generally assumed to have no donor ability.

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I. HYDROGEN BONDING OF INORGANIC OXYCHLORIDES

Robert Steinman

May 5, 1942

Considerable work has been done on the donor ability of oxygen and nitrogen containing organic compounds with potential acceptor solvents. However the donor ability of inorganic compounds, specifically the inorganic acid chlorides, with compounds containing an acceptor hydrogen to form the C-H ←-O linkage had not yet been investigated. In order to evaluate the influence of the highly negative chlorine atoms in the acid chlorides, it also became necessary to compare the observed effects with those of certain related organic compounds. The experimental study involved the determination of the heats of mixing of phosphoryl chloride, sulfuryl chloride, thionyl chloride, diethyl carbonate, diethyl sulfite, diethyl sulfate, and propionly chloride with chloroform and with carbon tetrachloride according to the method described by Zellhoefer and Copley (2).

The high heats of mixing of the inorganic acid chlorides with chloroform as acceptor solvent, in comparison to the negligible heat effect observed upon mixing the same compound with carbon tetrachloride gives definite evidence of hydrogen bonding. The influence of the chlorine atoms in decreasing the donor ability of the semi-polar oxygen atoms in forming hydrogen bonds was verified by substituting ethoxy groups for the chlorine atoms. Higher heats of mixing with chloroform were observed in the case of the esters than with the corresponding acid chlorides. This substantiates the postulate of Glasstone (1) that the electron attracting nature of the chlorine atoms decreases the donor ability of the oxygen atom.

References

(1) Glasstone, Trans. Faraday Soc., 33, 200 (1937).
(2) Zellhoefer and Copley, J. Am. Chem. Soc., 60, 1343 (1938).

II. PREPARATION, PROPERTIES, AND REACTIONS OF THE PHOSPHONITRILIC CHLORIDES

A. Preparation

The Schenck and Romer (1) method of preparing the phosphonitrilic chlorides by heating phosphorus pentachloride with ammonium chloride in s-tetrachloroethane, although the best so far devised, has several distinct disadvantages. Each preparation requires a) twenty to twenty-four hours of refluxing, b) the removal of the solvent by vacuum distillation, and c) washing with benzene to remove the oily polyhomologs. A simple and rapid method of preparation of the phosphonitrilic chlorides has been devised by the author and involves heating an intimate mixture of phosphorus pentachloride and excess ammonium chloride at temperatures between 130-150°C. The reaction proceeds in accordance with the equation

$$PCl_5 + NH_4Cl = (PNCl_2)_x \quad \text{where } x = 3,4, \text{ and higher polyhomologs.}$$

The trimer and tetramer are selectively extracted with petroleum ether; the oily homologs, by benzene, chloroform or carbon tetrachloride.

Phosphonitrilic chloride is not formed when phosphorus pentachloride and triphosphorus pentanitride are heated up to temperatures of 225°C.

B. Separation

A successful separation of trimeric from tetrameric phosphonitrilic chloride ban be achieved only by a process involving fractional vacuum distillation, followed by crystallization and sublimation. The vacuum distillation results in trimer and tetramer rich fractions; the crystallization from 100 per cent acetic acid gives products pure enough for chemical purposes; but only sublimation under reduced pressure yields products suitable for physical-chemical measurements.

C. Ammonolysis

Ammonolysis of the trimeric and tetrameric phosphonitrilic chlorides with liquid ammonia results in the formation of the respective phosphonitrilamides. Deammonation of these amides apoears to be irreversible and takes place progressively at temperatures up to 230°C. The rate of deammonation increases with temperature; no apparent difference in the rates ofdeammonation of the trimeric and tetrameric phosphonitrilamides could be observed. The products are ammonia and presumably phospham.

$$\left[PN(NH_2)_2\right]_x = (PNNH)_y + NH_3 \quad \text{where } x = 3, \text{or } 4 \text{ and } y = \text{higher polymers (?)}$$

No evidence was obtained for the formation of stable intermediate products.

D. Aminolysis

With primary and secondary amines, the phosphonitrilic chlorides may undergo aminolysis directly, in solution, or in pyridine, and rather definite compounds are obtained. The N-substituted phosphonitrilamides of the aliphatic and cycloaliphatic amines appear to be varied in nature for duplicate analyses of the same compounds never agreed. This may possibly be due to the difficulty in replacing all the chlorine atoms with amine groups, or to the formation of a very stable phosphorus-nitrogen derivative which is not decomposed during analysis. Reactions of the trimeric and tetrameric phosphonitrilic chlorides and of the polymeric elastomer were carried out using the following amines: aniline, cyclohexylamine, dicyclohexylamine, n-octylamine, n-hexylamine, diethylamine, n-isobutylamine, and n-butylamine.

E. Vapor Pressure

The apparatus and method employed in measuring the vapor pressures of trimeric phosphonitrilic chloride were those previously employed by Laubengayer and Schirmer(2).

On the basis of measured values the change in vapor pressure of the solid with respect to temperature may be represented by the equation

$$\log p = 11.1869 - 3.9776(1/T)$$

The vapor pressure of the liquid trimer over the temperature range 114° (the melting point) to 190° is given by the equation

$$\log p = 8.3568 - 2.8796(1/T)$$

The melting point of trimeric phosphonitrilic chloride as calculated from the intersection of these equations is 114.9°. This agrees well with the value 114° reported by other investigators (1,3). The boiling point obtained by extrapolation of the liquid-vapor curve to 760 mm. pressure is 252.7°, and is in fair agreement with the value 256° reported by Stokes (3).

The molar heat of vaporization calculated from the slope of the liquid-vapor curve is 13.17 kilocalories. The molar heat of sublimation calculated from the slope of the solid-vapor curve is 18.20 kilocalories, and the molar heat of fusion obtained by difference is 5.03 kilocalories.

References

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LIQUID-LIQUID EXTRACTION OF RARE EARTHS

Howard Leventhal May 12, 1942

A. Introduction

All methods which have thus far been devised for the separation of rare earths are incomplete and time consuming. Such methods as are employed may be classified under several headings:

1. Fractional Crystallization
2. Fractional Precipitation
3. Methods involving valence changes
4. Methods making use of physical and physico-chemical procedures

B. Historical

Only two previous investigations[1,2] have concerned themselves with the possibilities of a successful separation by means of liquid-liquid extraction.

C. Experimental

The method of operation employed was that of cocurrent extraction.

D. Conclusions

1. The order of extractability of rare earth salts is given by the following series

$$SCN^- > ClO_4^- > NO_3^- > Cl^-$$

2. The selectivity of the butyl alcohol varies with the molarity of the aqueous phase, and the rare earth salt used.

3. The amount extracted increased with molarity from one tenth to three tenths molar.

4. At concentrations above two tenths to three tenths the amount extracted tends to become independent of the molarity.

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SOME COORDINATION COMPOUNDS OF COBALT AND CHROMIUM WITH ORGANIC DIAMINES

J.B.Work May 19, 1942

It is well known that ethylenediamine and metal salts form a wide variety of coördination compounds which owe their stability to the presence of five-membered chelate rings. Similar compounds having larger rings, however, are both more difficult to prepare and less stable than those containing ethylenediamine or its derivatives.

The present study was designed to examine the coördination ability of diamines which would give rise to chelate rings of six or more atoms. In the course of the investigation it was noted that Bjerrum[1] had used activated charcoal to catalyze the formation of hexammine cobaltic chloride and triethylenediamine cobaltic chloride. It has now been shown that many other reactions in the field of coördination compounds are subject to catalysis by such materials of large surface area as activated carbon, Raney nickel, and silica gel. The fundamental type of reaction catalyzed is the entrance of nitrogen (of either nitro or amine groups) into the coördination sphere of a metal ion.

It has been shown that activated carbon catalyzes the following reactions:

1- <u>trans</u> $[Co\ en_2\ Cl_2]Cl + 2\ NaNO_2 \rightarrow [Co\ en_2(NO_2)_2]Cl + 2NaCl$
2- <u>levo</u>-<u>cis</u> $[Co\ en_2\ Cl_2]Cl$ + excess $NaNO_2 \rightarrow$ <u>dextro</u>-<u>cis</u> $[Co\ en_2(NO_2)_2]NO_2 + 3\ NaCl$
3- <u>trans</u> or <u>cis</u> $[Co\ en_2\ Cl_2]Cl$ + excess $NH_4OH \rightarrow$ <u>trans</u> (+ <u>cis</u>) $[Co\ en_2(NH_3)_2]Cl_3 + H_2O$
4- <u>dextro</u>-<u>cis</u> $[Co\ en_2(NH_3)Cl]Cl_2$ + excess $NaNO_2 \rightarrow$ <u>dextro</u>-<u>cis</u> $[Co\ en_2(NH_3)(NO_2)]Cl_2 + NaCl$
5- <u>cis</u> $[Co\ en_2(NH_3)Cl]Cl_2$ + excess $NH_4OH \rightarrow$ <u>trans</u> (+ <u>cis</u>) $[Co\ en_2(NH_3)_2]Cl_3 + H_2O$
6- $[Co\ en_2(NH_3)_2]Cl_3$ + excess $NaNO_2$ + heat $\rightarrow 2\ NH_3 + [Co\ en_2(NO_2)_2]NO_2$
7- $4\ CoCl_2 + 10\ tn + 2(tn{\cdot}2HCl) + O_2 \rightarrow 4\ [Co\ tn_3]Cl_3 + 2H_2O$
8- $4\ CoCl_2 + 12\ dan + 4\ HCl + O_2 \rightarrow 4\ [Co\ dan_3]Cl_3 + 2\ H_2O$
9- $CrCl_3{\cdot}6H_2O + 3\ en$ + heat $\rightarrow [Cr\ en_3]Cl_3 + 6\ H_2O$
10- $[Co\ en_2\ Cl_2]Cl + tn \rightarrow [Co\ en_2\ tn]Cl_3$
11- $[Co\ en_2\ Cl_2]Cl$ + diabip $\rightarrow [Co\ en_2\ diabip]Cl_3$
12- $[Co\ en\ tn\ Cl_2]Cl + dan \rightarrow [Co\ en\ tn\ dan]Cl_3$
13- $[Co(NH_3)_5Cl]Cl_2 + NH_4OH \rightarrow [Co(NH_3)_6]Cl_3 + H_2O$
14- $Na_3[Co(NO_2)_6] + NH_3 \rightarrow [Co(NH_3)_3(NO_2)_3] + 3\ NaNO_2$
15- $NH_4[Co(NH_3)_2(NO_2)_4] + NH_3 \rightarrow [Co(NH_3)_3(NO_2)_3] + NH_4NO_2$
16- $[Co(NH_3)_6]Cl_3 + H_2O$ + heat $\rightarrow Co(OH)_3 + Co(OH)_2 + NH_3 + NH_4Cl$
17- $[Co(NH_3)_6]Cl_3 + 3\ NaNO_2$ + heat $\rightarrow [Co(NH_3)_3(NO_2)_3] + 3\ NaCl + 3\ NH_3$

(In the preceding equations "en" represents ethylenediamine, "tn" designates trimethylenediamine, "dan" stands for diaminoneopentane, and "diabip" refers to 2,2'-diaminobiphenyl.)

The reactions cited above were used as the bases for the development of methods for the preparation and study of $[Co\ tn_3]Cl_3$, $[Co\ dan_3]Cl_3$, $[Co\ en_2\ tn]Cl_3$, and $[Co\ en\ tn\ dan]Cl_3$. The first two of these salts, in which three six-membered rings are present, were found to possess a pinkish-yellow color in contrast to the orange tint usually displayed by luteo compounds. The only comparable case is that cited by Jaeger[2] in reference to tri-[<u>trans</u> cyclopentylenediamine] cobaltic chloride. As with the iodide of the latter series, $[Co\ tn_3]I_3$ has the normal orange color. Since only the chloride of

these ions shows the anomalous color, and then only in the solid state, it is probable that the irregular color is caused by some factor in the crystal structure.

Using catalysis by activated charcoal, improvements were effected in the methods for the preparation of [Co $en_2(NO_2)_2$]Cl, [Co $en_2(NH_3)_2$]Cl_3, [Co en_2 diabip]Cl_3, and [Cr en_3]Cl_3. The almost instantaneous reactions which this catalyst makes possible were used in an unsuccessful search for a Walden Inversion in the reactions of [Co $en_2(NH_3)$Cl]Cl_2 and [Co en_2 Cl_2]Cl with sodium nitrite and ammonium hydroxide.

Werner[3] has discussed a large number of reactions which start with [Co en_2 Cl_2]Cl. A chart which is included in this thesis shows about twenty-five such reactions and also indicates some of the conversions that are readily catalyzed by charcoal.

The presence of activated carbon has been shown to catalyze the formation of [Co en_3]Cl_3 by disproportionation of [Co en_2 Cl_2]Cl in aqueous solutions containing methyl amine, isopropyl amine, aniline, pyridine, or decamethylenediamine. The suggestion has been made that the avoidance of aqueous solutions might eliminate this reaction. The experiments which resulted in these disproportionations were attempts to replace both of the coördinated chloro groups from [Co en_2 Cl_2]Cl by two molecules of a monoamine, or by diamines which would produce large chelate rings. Neither hexamethylenediamine nor decamethylenediamine could be made to form such rings. That 2,2'-diaminobiphenyl did replace the two chloro groups with the formation of [Co en_2 diabip]Cl_3, which Middleton[4] had prepared, may be ascribed to the fact that the relative positions of the amino groups are somewhat limited by their positions on the biphenyl structure. Although charcoal assisted in the preparation of [Co en_2 diabip]Cl_3 and of [Co en tn dan]Cl_3 from the respective dichloro salts, it did not cause the formation of [Co en tn diabip]Cl_3 although similar methods were used in seeking the latter compound.

Methods were developed for the preparation of <u>trans</u> [Co tn_2Cl_2]Cl, [Co dan_2 Cl_2]Cl, and [Co en tn Cl_2]Cl. These compounds were compared with [Co en_2 Cl_2]Cl and the differences in properties were discussed. Grinding these dichloro compounds with moist silver carbonate results in the formation of the corresponding carbonato compounds. Treatment of these salts with a solution of hydrogen chloride in a mixture of alcohol and ether yields the <u>cis</u> dichloro compounds. <u>Cis</u> [Co tn_2Cl_2]Cl and <u>cis</u> [Co dan_2 Cl_2]Cl rearrange to the <u>trans</u> form in the solid state, whereas <u>cis</u> [Co en tn Cl_2]Cl is stable.

Werner and Lindenberg[5] found <u>trans</u> [Co tn_2 Cl_2]Cl to change from green to purplish-red almost immediately upon dissolving in water. This reaction, which is also shown by <u>trans</u> [Co dan_2 Cl_2]Cl, is probably due to the formation of <u>trans</u> chloro aquo salt rather than <u>cis</u> dichloro, since the latter is so extremely unstable.

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1942-1943.

THE METAL CARBONYLS

Fred Basolo Oct. 13, 1942

I. History

A. Ludwig Mond - 1890

discovered $Ni(CO)_4$

B. Marcellin Berthelot - June 15, 1891

announced an iron carbonyl. Fourteen days later Mond and Quincke disclosed its independent discovery. One year later Mond and Langer gave the compound a formula of $Fe(CO)_5$.

C. Mond, Hirtz and Cowap - 1908

$Co_2(CO)_8$, $Mo(CO)_6$, $Ru(CO)$, $Ru(CO)_2$, and $Co_4(CO)_{12}$

D. Job and Coworkers

prepared $Cr(CO)_6$ and $W(CO)_6$ by the action of carbon monoxide on solutions of metal salts and Grignard reagents.

II. Preparation

A. Direct combination

$$xMe + yCO \rightleftharpoons Me_x(CO)_y$$

All of the metal carbonyls, except that of chromium, have been prepared by direct combination of the metal with carbon monoxide.

B. From metal salts

Carbonyls are also prepared from metal salts and carbon monoxide in the presence of quite a variety of combinations of reagents.

III. Constitution

A. Concepts which have been proposed

1. Ludwig Mond - 1892

suggested a ring structure with the metal as one member of the ring.

2. A.J.F. da Silva - 1896

proposed a combination of ring and branch chain for $Fe(CO)_5$

3. Werner - 1909

said the carbon monoxides are all coordinated to the metal

4. Blanchard and Gilliland - 1926

coordinate only four carbon monoxides to the metal, using up the excess by CO:CO bridges.

5. Reihlen - 1928

differs from the other concepts in that he considers the carbonyl groups as constituents of hypothetical acids

6. Manchot and Hieber - 1928

agree with Werner

B. Most widely accepted concept

1. Werner-Hieber-Manchot theory

M:C:::O: or M::C::O::

2. Sidgwick

proposed an equation to correlate known metal carbonyls as well as predict existence of others.

$$G - \frac{Xm + 2y}{X} = X - 1$$

G = at. no. of next inert gas; m = at. no. of metal; X = no. of metal atoms in molecule; y = no. of carbonyl group in the molecule.

3. Polar valence in volatile carbonyls
   a. Ni = 0 in $Ni(CO)_4$
   b. Co = -1 in $Co(CO)_3NO$ and $(CO)_3CoCO{:}H$
   c. Fe = -2 in $Fe(CO)_5$, $Fe(NO)_2(CO)_2$, $Fe(CO)_4H_2$, and $[Fe(CO)_4]_3$

IV. Properties
   A. General Behavior
      Metal carbonyls resemble organic compounds. They are not salt-like; are poor conductors of electricity; and are diamagnetic. (See Table I).
   B. Chemical Reactions
      1. Addition
         $Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_5X_2$
      2. Substitution
         $Ni(CO)_4 + X_2 \longrightarrow NiX_2 + 4CO$
         $Ni(CO)_4 + \text{o-phthr} \longrightarrow Ni(CO)_2\text{o-phthr} + 2CO$
         $Fe(CO)_5 + 2NO \longrightarrow Fe(NO)_2(CO)_2 + 3CO$
         $\downarrow$ o-phthr
         $Fe(NO)_2\text{o-phthr} + 2CO$
      3. With a Grignard reagent
         $Ni(CO)_4 + 4C_6H_5MgBr \longrightarrow Ni + 4\ CO\begin{matrix}-MgBr\\ \backslash C_6H_5\end{matrix}$
      4. With weak base to give hydrides
         $3Co(CO)_4 + 2H_2O \longrightarrow 2HCo(CO)_4 + Co(OH)_2 + 4CO$

V. Industrial Significance
   A. Refining of nickel
      The process involves the formation of $Ni(CO)_4$ which boils off from the impure residue and then is decomposed to give pure nickel
   B. $Fe(CO)_5$ as antiknock - "Motalin"
      1. Advantages over lead tetraethyl
         a. Less toxic, b. exhaust products less toxic, c. completely soluble in gasoline, d. as good an antiknock
      2. Disadvantage
         $2Fe(CO)_5 \xrightarrow{\text{light}} Fe_2(CO)_9 + CO$
   C. Poisonous
      these compounds are toxic
   D. Artificial gases
      Iron carbonyls are formed in handling of artificial gas
   E. Fe_2O_3 from $Fe(CO)_5$
      used as polishing powder, coloring material, etc.
   F. Carbonyl Iron - Very pure
   G. Catalyst from carbonyls
      finely divided nickel from $Ni(CO)_4$
   H. Miscellaneous suggestions
      1. Blue prints using instability of $Fe(CO)_5$ in light
      2. Preparation of hydrocarbons
      3. Plating by decomposing metal on hot surface

VI. More Recent Trends
   A. Iron Carbonyls
      1. Iodides
         $Fe(CO)_2I_2$, $Fe(CO)_2I$, and FeI prepared using $Fe(CO)_5$ and I_2
      2. Halides
         $Fe(CO)_4IBr$, $Fe(CO)_4ICl$, $Fe(CO)_2I_2py_2$, $Fe(CO)_4SOCl_2$, $Fe(CO)_4SbCl_4$ and $Fe(CO)_4SnCl_4$ have been prepared and found that their stability increases as follows: $M = Fe(CO)_4$ $MCl_2 < Fe(CO)_2Cl_2 < MCl_2SbCl_5 < MCl_2SnCl_2 < MBr_2 < MIBr < MI_2$.

3. Organic sulfur compounds
   The action of a sulfide on $[Fe(CO)_4]_3$ gave: $(OC)_3FeSC_{10}H_7$, $[(OC)_3FeSCH_3]_2$, $[(OC)_3FeC_2H_5]$

B. Iridium halide carbonyls
   $IrX(CO)_3$, $IrX_2(CO)_2$, and $Ir(CO)_3$ were prepared by the action of carbon monoxide on the anhydrous salts at varying temperatures.

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TABLE I

Some Properties of Metal Carbonyls

Metal Carbonyl	Discoverer and date	Color and state	M.P.	B.P.	Vapor Press. mm.	Sp.Gr.	Temp. of formation	Decomposition
$Ni(CO)_4$	Mond, Langer, Quincke 1890	Water-clear liquid	-25°	43.2°	238 (15°)	1.31 (20°)	30-50° (1 atm.)	to CO and Ni above 50° at 1 atm. at 0° in vac.
$Co_2(CO)_8$	Mond, Hirtz, Cowap 1908	Orange crystals	51°	D.52°	0.72 (15°)	1.73	220° at 150 atm.; 150° at 40 atm.	to CO and Co above 60°; to Co and $Co_3(CO)_{12}$ at 50-60°
$Co_3(CO)_{12}$	Mond, Hirtz, Cowap 1908	Jet black crystals	D above 60°		-	-	60° from $Co_2(CO)_8$	to CO and Co above 60°
$Fe(CO)_5$	Berthelot (Mond) 1891	Water-clear liquid	19.5	104.6	25.9 (16°)	1.45 (20°)	173° at 200 atm.	to $Fe_2(CO)_9$ by light to CO and Fe above 130°
$Fe_2(CO)_9$	Mond, Langer 1891	Golden Plates	D. at 100°		-	2.09 (18°)	Light on $Fe(CO)_5$ at room temp.	to $Fe(CO)_5$, Fe and CO at 100°; to $Fe_3(CO)_{12}$ and $Fe(CO)_5$ in soln. at 95°
$Fe_3(CO)_{12}$	Dewar, Jones 1905	Dark green tables	D. at 145°		-	1.996 (18°)	From $Fe_2(CO)_4$ at 60°	to Fe and CO at 150°
$Cr(CO)_6$	Job, Cassol 1926	Colorless crystal	Sublimes at room temp.		60.6 (100.4°)	-	0-4°	to CO and Cr by light; to to CO and Cr at 200°; explodes at 210°

TABLE I (cont.)

$Mo(CO)_6$	Mond, Hirtz, Cowap 1908	Colorless crystal	Sublimes at 30-40°	43.2 (100°)	1.96 (15°)	200° at 200-250 atm.	to CO and Mo above 150°
$W(CO)_6$	Job, Rouvillois 1928	Colorless crystal	Sublimes at 50°	14.4 (100°)	-	0-4°	to CO and W above 100°
$Ru(CO)$	Mond, Hirtz, Cowap 1908	Orange-yellow crystal	- -	-	-	300° at 300-400 atm.	to Co and Ru on heating

SULFAMIC ACID

John M. Stewart October 20, 1942

Sulfamic acid was first prepared and isolated about 65 years ago by Berglund by hydrolysis of imido-disulfonate salts with dilute acids.

$$N(SO_3K)_3 + 2HOH \longrightarrow NH_2SO_2OK + 2KHSO_4$$

It was called amidosulfamic acid and several other laboratory preparations were discovered for it.

(1) Ammonalysis of sulfuric acid and related compounds:

$$ClSO_3K + 2NH_3 \longrightarrow NH_2SO_3K + NH_4Cl$$

(2) Nitridation of sulfur dioxide, sulfurous acid, sulfites, and hydrosulfites. For example, the Raschig method:

$$NH_2OH + SO_2 \longrightarrow NH_2SO_2OH$$

A new process discovered independently in this country and Germany in 1938 has made sulfamic acid available in carload lots and commercialization has rapidly expanded.

$$C{=}O(NH_2)_2 + SO_3 \cdot H_2SO_4 \longrightarrow \left(\begin{array}{c} H \\ | \\ N - SO_3H \\ | \\ C = O \\ | \\ N - SO_3H \\ | \\ H \end{array}\right) \xrightarrow{H_2O} 2NH_2SO_3H + CO_2$$

Sulfamic acid is a crystalline solid melting with decomposition at 205° C. It is colorless, odorless, non-volatile and non-hygroscopic. It is soluble in water, the solubility increasing greatly with temperature and decreasing with content of sulfuric acid. It is soluble in nitrogenous solvents such as formamide and liquid ammonia. The crystal structure is orthorhombic and Baumgarten suggests that the formula $H_3^+NSO_2\text{-}O^-$ represents the solid form. In a recent study of solutions of potassium sulfamate Brown and Cox showed the ion to be definitely $(NH_2SO_3)^-$ and not $(NHSO_2OH)^-$, and concluded that the three oxygen atoms and the nitrogen atom are arranged in almost tetrahedral configuration around the sulfur atom.

Sulfamic acid is highly ionized in aqueous solution, and its conductometric and pH measurements place it between phosphoric and hydrochloric acids in acid strength. It is recommended as a primary standard in acidimetry and has been found superior to benzoic acid, succinic acid, potassium acid phthalate, etc. It can be titrated using indicators with pH transition range between 4.5 and 9. It is not used as standard solution due to hydrolysis on long standing or heating.

$$NH_2SO_3H + HOH \longrightarrow HOSO_3H + NH_3 (\text{or} NH_4HSO_4)$$

Chlorine, bromine, and chlorates oxidize sulfamic acid in the cold to sulfuric acid, while permanganate, chromic acid and ferric chloride do not oxidize it.

N-chloro sulfamic acid, though formed in the cold by action of HOCl on sulfamic acid is unstable. Some of its salts are stable and have been prepared.

$$NH_2SO_3H + HOCl \longrightarrow ClNHSO_3H + H_2O$$

Sulfamyl chloride also has not been prepared, though many attempts have been made to do so. It is believed to be so unstable that, when formed, goes immediately over into trisulfimide.

$$3NH_2SO_2Cl \longrightarrow (NHSO_2)_3 + 3HCl$$

Boric acid was first prepared and isolated about 80 years ago by [illegible] designed to substitute at [illegible]-hydroxyl acid with dilute acid [illegible] $B(OH)_3 + 2HOC \longrightarrow B(OC)_3 + 3H_2O$. It was called orthoboric acid and several other laboratory preparations were discovered thereafter:

(1) Hydrolysis of alkali acid and related compounds:

$$Cl_3B + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$

(2) Attraction of water from alcohol, glycerol, acid, alkali, and hydrogen.

For example, the basic method

$$BH_4Cl + 3O_2 \longrightarrow BH_3O_3 + HCl$$

A new process discovered independently in this study and [illegible] 1948 has made boric acid available in crystal form at an economical price [illegible] the purity expected.

Boric acid is a crystalline solid melting with decomposition at [illegible] 0. It is soluble, colorless, odorless, tasteless and non-hygroscopic. It is stable to water. The solubility increases greatly with temperature and decreases with content of alkali acid. It is soluble in [illegible] solvents and is formable and [illegible]. The crystal structure is orthorhombic and [illegible] that the formula [illegible] represents the solid form. In a recent study of solubility of potassium sulfate, Stewart and Cox showed the [illegible] BH_3O_3 and not $(BHO_2)_n$, and concluded that the [illegible] of the stronger acids are strongest in [illegible] neutral coefficients [illegible] the weaker acids.

Boric acid is very soluble in aqueous solution, and its saturation and [illegible] plots is between [illegible] and [illegible] boric acid in acid [illegible]. It is recommended as a primary standard [illegible] and has been found superior to [illegible] acid, sodium carbonate, [illegible] sulfate, etc. It can be titrated using indicators [illegible] of titration range between 4.0 and 9. It is not used as standard [illegible] due to difficulties in long standing in [illegible].

$$BH_3O_3 + NaOH \longrightarrow NaBO_2 + BH_4[O_2BO_2(OH)_2]$$

Glycerin, however, has [illegible] boric acid to the [illegible] acid, making [illegible], thereby acid and ferric [illegible] not [illegible].

Tertiary alkyl acid, [illegible] formed in the [illegible] to [illegible] so boric acid is [illegible]. Some of the [illegible] have been prepared.

$$BH_3O_3 + ROH \longrightarrow BH(OR)_2 + H_2O$$

Tertiary alkyl borate also has not been prepared, though many attempts have been made to do so. It is believed to be an unstable [illegible], since [illegible] easily over into [illegible].

$$3BH_3O_3 \longrightarrow (HBO)_3 + 3H_2O$$

Sulfamic acid reacts rapidly and quantitatively with nitrites:

$$NH_2SO_2OH + KNO_2 \xrightarrow{H^+} KHSO_4 + N_2 + H_2O$$

This is a very useful reaction for the qualitative and quantitative determination of either sulfamic acid or of nitrites, especially in the presence of nitrates. This reaction is utilized in separating the lanthanum rare earths from the yttrium group. It is valuable commercially in elimination of excess nitrite employed in diazotization reactions for dye and pigment manufacturing. It finds further use in analytical procedures for determination of dissolved and biochemical oxygen demand in sewage treatment and river pollution studies.

Concentrated nitric acid reacts with sulfamic acid to generate pure nitrous oxide: $NH_2SO_3H + HNO_3 \rightarrow H_2SO_4 + H_2O + N_2O\uparrow$

Sulfamic acid combines readily with basic metal oxides, hydroxides, and carbonates to yield the corresponding salts. Amphoteric or acidic metal oxides react slowly or not at all. Bismuth, antimony, and arsenic salts are not known. All known sulfamate salts, with the exception of one basic mercury salt, are soluble in water.

Ammonium sulfamate is obtained by dissolving sulfamic acid in liquid ammonia. The solution is definitely acidic, and acts as a dibasic acid forming a disodium and a dipotassium salt.

Sulfamates, especially ammonium sulfamate, are valuable fireproofin agents.

Advantages have been observed in the use of sulfamic acid instead of sulfuric in various tanning processes. It gives a finer, silkier grain with better working qualities.

Reports on the use of sulfamic acid and ammonium sulfamate as herbicidal agents are highly favorable. Ammonium sulfamate has much more effective weed-killing action than ammonium sulfate, ammonium thiocyanate, sodium chloride and calcium chloride. Other advantages to its use as herbicide are the following: (1) Decomposed rapidly by bacteria in the soil and so no danger of long-time soil sterilization. (2) In physiological tests it was found non-toxic to animals. (3) Doesn't possess fire hazard associated with certain weed killers.

Nitrogen-Substituted Derivatives of Sulfamic Acid

These are prepared by several general methods.

(A) Aminolytic reactions - involves use of some form of hexavalent sulfur for either of two processes: (1) interposition of a bivalent $-SO_3$ group between the nitrogen and hydrogen in primary and secondary amines, or amides.

$$R_2NH + SO_3 \rightarrow R_2NSO_3H$$

(2) the addition of SO_3 through a coordinate link to the nitrogen in a tertiary amine

$$R_3N + SO_3 \rightarrow R_3N^+ \cdot SO_3$$

Reactions in which free sulfamic acid is aminolyzed by primary aliphatic or aromatic amines give products varying with the basicity of amine.

$$RNH_2 + NH_2SO_3H \rightarrow RNHSO_3H \cdot H_2NR$$
$$ArNH_2 + NH_2SO_3H \rightarrow ArNHSO_3NH_4$$

If the basicity is great enough, one gets the amine salt of the N-substituted acid. If basicity low, one gets the ammonium salt of the alkyl or aryl sulfamate.

Sulfamic acid reacts rapidly and quantitatively with nitrites:

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Reactions in which free sulfamic acid is aminolyzed by primary aliphatic or aromatic amines give products varying with the basicity of the amine.

$$RNH_2 + NH_2SO_3H \longrightarrow RNHSO_3NH_4$$

$$ArNH_2 + NH_2SO_3H \longrightarrow ArNHSO_3NH_4$$

If the basicity is great enough, one gets the amine salt of the N-substituted acid. If basicity low,

(B) Nitridation reactions

The usual nitridizing agents are aromatic nitro compounds or hydroxylamine derivatives.

$$Ar\ NH_2 + SO_2 \xrightarrow[\text{tube}]{\text{sealed}} Ar\ NHSO_3H$$

$$Ar\ NO_2 + NaHSO_3 \longrightarrow Ar\ NHSO_3Na$$

(C) Miscellaneous methods of preparation include:

(1) N-acylation

$$RCOCl + NHRSO_3H \xrightarrow{\text{pyridine}} RCON\begin{matrix}\diagup SO_3H \\ \diagdown R\end{matrix}$$

(2) N-alkylation or arylation

$$Ar\ CHCl_2 + NH_2SO_3H \longrightarrow Ar\ CH{=}NSO_3H$$

$$RCHO + NH_2SO_3\text{-Metal} \longrightarrow RCH{=}NSO_3\ \text{Metal}$$

All metallic and amine salts of N-substituted sulfamic acid are solids, as are the free acids where they are known.

Salts of the types $RR'NSO_3H$ and $Ar\ NHSO_3H$ are fairly stable toward alkali, whereas compounds such as $RCH{=}NSO_3H$ are not. As a class sulfamic acids are not stable in acid solution. N-aryl sulfamic acids are extremely sensitive to acid and very few are known in the free state.

Free acids of the type $RNHSO_3H$, where R is either alkyl or aryl, dissolve in cold concentrated nitrous acid or alkali nitrites. On standing N-Nitroso salts of the type $RN(NO)SO_3M$ precipitate from solution. The nitroso salts are sensitive andmay explode on heating.

Reactions of Sulfamic Acid with Organic Substances

Primary alcohols react smoothly on heating and yield the corresponding esters of ammonium acid sulfate.

$$CH_3OH + NH_2SO_3H \longrightarrow \begin{matrix} NH_4\text{-}O \diagdown \\ CH_3\text{-}O \diagdown \end{matrix} S \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$$

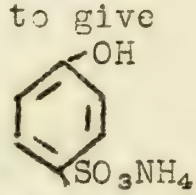
Alkylation of the acid by ordinary methods yields esters of dialkylsulfamic acid, $ROSO_2NR_2$, which readily rearrange if the R groups are small into a betaine structure, $R_3N{\cdot}SO_3$. Only one ester of an N-mono substituted sulfamic acid is recorded in the literature; it is N-benzyl benzyl sulfamate, $C_6H_5CH_2NHSO_3CH_2C_6H_5$. It is stable, doesn't rearrange on heating, and on alkaline hydrolysis yields N-benzyl sulfamic acid.

Aldehydes and ketones react with salts of sulfamic acid giving salts of the following type.

$$RCHOH{\cdot}NHSO_3\text{-Metal} \quad \text{or} \quad RCH{=}NSO_3\text{-Metal}$$

Phenols, naphthols, etc. react under suitable conditions to give aromatic sulfonated derivatives.

$$C_6H_5OH + NH_2SO_3H \xrightarrow{100^\circ} \begin{matrix} O \\ O \end{matrix} \!\!= S \begin{matrix} \diagup OC_6H_5 \\ \diagdown ONH_4 \end{matrix} \xrightarrow{150^\circ}$$



Aromatic amines react much the same yielding intermediate compound first, which rearranges on heating.

$$C_6H_5NH_2 + NH_2SO_3H \longrightarrow C_6H_5NH_2{\cdot}HSO_3NH_2$$

$$C_6H_5NH_2{\cdot}HSO_3NH_2 \xrightarrow{\Delta} C_6H_5NHSO_3NH_4 \xrightarrow{\Delta} pNH_2C_6H_4SO_3NH_4$$

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THE CHEMISTRY OF THE CHLORITES.

A. L. Oppegard October 27, 1942

I. Introduction
   A. Increased commercial importance has promoted research.
   B. The study of chlorites is complicated by their similarity to the other oxy-chlorine compounds.

II. Formation and Production
   A. Historical
      1. Gay-Lussac and others noted the formation from bleaching powder.
      2. Davy and Millon prepared them from chlorates and chlorine dioxide.
   B. From hypochlorites and hypochlorous acid.
      1. Chlorites intermediate in chlorate formation.
      2. Light an important factor - optimum exposure.
   C. From chlorates and ClO_2.
      1. Never accomplished directly, ClO_2 an intermediary.
      2. Production of ClO_2. Acid plus chlorate with careful control.
         a. $2KClO_3 + 2(COOH)_2 \rightarrow 2ClO_2 + CO_2 + (COOK)_2 + H_2O$

         b. $3KClO_3 + 3H_2SO_4 \rightarrow 2ClO_2 + HClO_4 + H_2O + 3KHSO_4$

            Water or some inert material is added as a diluent. It is said to be used commercially.
      3. Absorption of ClO_2 in alkaline solution
         a. Original procedure

            $2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$

         b. In presence of a reducing agent.

            $2ClO_2 + Na_2O_2 \rightarrow 2NaClO_2 + O_2$

         c. Mixtures of Cl_2 and ClO_2 must be separated before absorption.

III. Existence and general properties.
   A. Chlorites prepared.
      Many simple and complex chlorites have been prepared by Levi and his coworkers. Most of these are listed in Gmelin.
   B. General properties. (Mainly for sodium chlorite.)
      1. Forms
         $NaClO_2 \cdot 3H_2O$
         $NaClO_2$ - non-hygroscopic.
      2. Quite stable for storage - dry or solution.
      3. Percussion - will explode in the presence of grease.
      4. Same precautions for chlorates must be observed also for chlorites.

IV. Reactions of the Chlorites.

A. Decomposition
   1. Seems to be inherent in the chlorite itself.
   2. Presence of chlorides and chlorates has little effect.
   3. Acid solutions hasten decomposition.

$$4HClO_2 \longrightarrow 2ClO_2 + HClO_3 + HCl + H_2O$$

B. With chlorine and hypochlorites.
   1. Hypochlorites - ClO_2 primary product followed by:

$$2ClO_2 + HClO + H_2O \longrightarrow 2HClO_3 + HCl$$

   2. Chlorine - rapid, quantitative reaction

$$NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + NaCl$$

   3. Products are dependent on the pH of the solutions.
   4. Other common oxidizing agents will also liberate ClO_2.

C. Reducing agents.
   1. May also liberate ClO_2
   2. Formaldehyde in acid solution gives CO_2 and ClO_2.
   3. Quantitative reaction with iodides and sulfites can be used for their determination.

D. Bleaching action
   1. Chlorite, not ClO_2, does the bleaching.
   2. Carbon to carbon bonds are not attacked by chlorite, resulting in greater tensile strength.
   3. Chlorites act on the material to be removed, not the cellulose.

E. Oxidizing action
   1. Moderately strong oxidizing agent in acid solution.

pH 4 ..... 0.79 volts
pH 9 ..... 0.66 volts

   2. Suggested as a possible oxidizing agent for various selective oxidations in organic chemistry.

V. Uses of the Chlorites.

A. Bleaching
   1. Advantage lies in the greater whiteness without loss of tensile strength.
   2. Used on paper pulp, cotton, rayon, linen, straw, wood surfaces, coarse fibers, etc.
   3. Sugar sirups.
   4. Oxidation of vat dyes, stripping of sulfur dyes.
   5. Solubilizing of starch in weaving and finishing operations, (textile industry).

B. Source of chlorine dioxide.
   Used in pulp and flour bleaching.

C. Poisons for chlorophyl bearing plants.

D. Analytical reagent. C.P. $NaClO_2$ available.

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REDUCTIONS BY SOLUTIONS OF METALS IN LIQUID AMMONIA

Arthur Mattern November 3, 1942

I. Historical
   A. Weyl (1864)
      1. Dissolved alkali metals in liquid ammonia
      2. Considered solution due to formation of compounds such as $NaNH_3$
   B. Seeley (1871)
      1. Found that sodium, potassium, lithium all dissolved in liquid ammonia
      2. Aluminum, magnesium, thallium, indium, mercury and copper found to be insoluble
   C. Gore (1872)
      1. Studied the solubility of various substances in liquid ammonia
   D. Cady (1896-8)
      1. Studied ammonates
      2. Determined conductivity of solutions of metals in liquid ammonia
      3. Found that many organic compounds were reduced by metals in liquid ammonia
   E. Franklin and Kraus (1898)
      1. Studied the solvent action of liquid ammonia

II. Solutions of metals in liquid ammonia
   A. Preparation
      1. Direct
      2. Electrolysis
   B. Solubility of metals
   C. Stability of solutions
   D. Color
      1. Blue in dilute solution
      2. Copper-red in concentrated solution
   E. Density
   F. Conductivity
   G. Reaction of ammonia with dissolved metals
      1. $Na + xNH_3 \longrightarrow Na^+ + e^-.(NH_3)_x$
      2. $Ca + (x + 6)NH_3 \longrightarrow Ca(NH_3)_6^{++} + e^-(NH_3)_x$

III. Experimental procedures
   A. Reactions at low temperatures
      1. Advantages
      2. Disadvantages
   B. Reactions under pressure
      1. Reactions in sealed tubes
      2. Reactions in an autoclave
      3. Advantages and disadvantages of each

IV. Types of reduction reactions
   A. Reactions with elements
      1. $K + O_2 \longrightarrow K_2O_2 \longrightarrow K_2O_3 \longrightarrow K_2O_4$
      2. $Na + S \longrightarrow Na_2S \longrightarrow Na_2S_x$
      3. $Na + 3P$ (excess) $+ 3NH_3 \longrightarrow NaP_3 \cdot 3NH_3$
         $6Na$ (excess) $+ 2P + 3NH_3 \longrightarrow Na_3P_2H_3 + 3NaNH_2$

B. Ammonium salts

1. $NH_4^+ + e^- \longrightarrow NH_3 + 1/2H_2\uparrow$

   May be used to bring reactions to completion

   $GeI_2 + 3NH_3 \longrightarrow GeNH + 2NH_4I$

   $2NH_4I + 2Na \longrightarrow 2NaI + 2NH_3 + H_2\uparrow$

C. Hydrides

1. $GeH_4 + Na \longrightarrow NaGeH_3 + 1/2H_2$

D. Oxides

1. $NO + Na \longrightarrow NaNO$
2. $N_2O + 2K + NH_3 \longrightarrow KNH_2 + KOH + N_2$

   $N_2O + 2KNH_2 \longrightarrow KN_3 + KOH + NH_3$

3. $2CO + K \longrightarrow K(CO)_2$ also $LiCO \equiv Ca(CO)_2$, $RbCO \equiv Ba(CO)_2$
4. $CO_2 + Na + NH_3 \longrightarrow H_2NCO_2Na + 1/2H_2\uparrow$

E. Halides (except salts)

1. $2NI_3 \cdot 3NH_3 + 6Na \longrightarrow 6NaI + N_2 + 6NH_3$
2. $BiI_3 + 6Na \longrightarrow Na_3Bi + 3NaI$

F. Salts

1. Simple

   (1) Reduction product is the free metal

   (a) $Na + AgCl \longrightarrow NaCl + Ag\downarrow$

   (b) $CuI + Na \longrightarrow Cu\downarrow + NaI$

   (c) $NiBr_2 + 2K \longrightarrow Ni\downarrow + 2KBr$

   (d) Properties of the free metal

   (2) Intermetallic compound formed

   (a) $9Na + 4Zn(CN)_2 \longrightarrow 8NaCN + NaZn_4\downarrow$

   (b) $CdI_2 + 3Na \longrightarrow NaCd + 2NaI$

   (c) $2Hg(CN)_2 + 5Ca \longrightarrow Ca_3Hg_2 + 2Ca(CN)_2$

   (3) Product takes part in additional reactions

   (a) $2Na + MnI_2 \longrightarrow 2NaI + Mn\downarrow$

   $2Na + 2NH_3 \xrightarrow{Mn} 2NaNH_2 + H_2\uparrow$

   $Mn + 2NaNH_2 \longrightarrow Mn(NHNa)_2 + H_2\uparrow$

   (4) Miscellaneous reactions

   $NaNO_2 + Na \longrightarrow Na_2NO_2$

2. Complex

   (1) $K_2Ni(CN)_4$ (excess) $+ K \longrightarrow K_2Ni(CN)_3 + KCN$ Bright red.

   $K_2Ni(CN)_4 + 2K$ (excess) $\longrightarrow K_4Ni(CN)_4$ yellow ppt.

G. Organic substances

1. Displacement of an equilibrium involving an organic compound, the solvent and an ammonium salt

   $RX + 2NH_3 \rightleftharpoons RNH_2 + NH_4^+ + X^-$

   $NH_4^+ + e^- \longrightarrow NH_3 + 1/2H_2\uparrow$

2. Displacement of hydrogen

   $RH + e^- \longrightarrow R^- + 1/2H_2$

3. Metal addition

   (a) To double bonds

   $R_{n-1}A = AR_{n-1} + 2e^- \longrightarrow R_{n-1}AAR_{n-1}^=$

   (n = valence of element A)

   (b) Addition to free groups

   $R_3C + e^- \longrightarrow R_3C^-$

4. Bond rupture

   $R_{n-1}AA'R'_{n'-1} + 2e^- \longrightarrow R_{n-1}A^- + R_{n'-1}A'^-$

5. Removal of halogen

   $RX + 2e^- \longrightarrow R^- + X^-$

6. Removal of other elements

   $C_6H_5NO_2 + 2Na \longrightarrow C_6H_5NO + Na_2O$

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HYDRAZOIC ACID AND ITS METAL AZIDES

C. G. Overberger November 10, 1942

I. Introduction

Hydrazoic acid belongs to that unique class of hydronitrogens which resemble the hydrocarbons in structure.

A. Peculiar points

II. Structure of hydrazoic acid and the azides

A. Emil Fisher prepared phenyl azide by the action of dilute alkali upon the corresponding nitrosohydrazine and on the basis of this reaction postulated the cyclic structure

$$C_6H_5 - N \begin{matrix} -N = O \\ -N = H_2 \end{matrix} \xrightarrow{-H_2O} C_6H_5 - N \begin{matrix} -N \\ \| \\ -N \end{matrix}$$

B. Structure accepted by Curtius

C. Pentavalent nitrogen theory

D. Langmuir first pointed out that cyanate and azides possess similar physical and chemical properties. Both KN_3 and KNCO crystallize in the tetragonal system and have approximately the same axiel ratios

E. Hendrick and Pauling

$$\ddot{N}::\ddot{N}::\ddot{N}: \qquad \ddot{N}:\ddot{N}:\ddot{N} \qquad :\ddot{N}:\ddot{N}:\ddot{N}:$$

F. Recent controversy

1. Difference between azide ion type and type possessing a covalent link between the nitrogen and an organic radical
2. Sidgwick's structures

$$R - N \begin{matrix} -N \\ \| \\ -N \end{matrix} \qquad R - N = N \rightleftharpoons N \quad R - N \leftarrow N = N$$

   a. Dipole measurements
   b. Parachor values
3. Hantzch's viewpoint
4. Sutton, Brockway and Pauling, and later workers.

III. History and preparation

A. First compound containing N_3 group was prepared by Peter Griess who obtained phenyl azide by treatment of benzenediazonium perbromide with aqueous NH_3

B. Other earlier workers (Fisher, Curtius, Dennis and Isham).

C. General preparations

1. Direct synthesis
2. Interaction of inorganic and organic derivatives of HONO upon hydrazine and its compounds involving diazotization of hydrazine or the hydrazinolysis of nitrous acid
   a. $N_2H_4 + HNO_2 \longrightarrow HN_3 + 2H_2O$ (Thiele)

   $$\begin{matrix} N_2H_4 \\ \text{or} \\ N_2H_4 \cdot H_2SO_4 \end{matrix} + \begin{matrix} HONO \\ \text{or} \\ C_5H_{11}ONO \end{matrix} \xrightarrow[\text{NaOH}]{\text{Na-OET or}} NaN_3$$

   $N_2H_4 + AgONO \rightarrow AgN_3$

   $N_2H_4 + NOCl \rightarrow HN_3$

   $N_2H_4 + NCl_3 \nearrow$

   b. Other examples
3. Oxidation of hydrazine
   a. Types of oxidation
4. Ammonlysis of nitrous acid and $NaNO_2$
   a. $N_2O + 2NaNH_2 \longrightarrow NaN_3 + NaOH + NH_3$
   b. HN_3 is an ammonitric acid, the NH_3 analogue of nitric acid In the fused state, the following reaction occurs

   $$NaNO_3 + NaNH_2 \xrightarrow{\text{fused}} NaN_3 + 3NaOH + NH_3$$

5. Oxidation of triazene and decomposition of higher hydronitrogens

a. $C_6H_5\text{-}NH\text{-}NH_2 + [O] \longrightarrow C_6H_5N_3 + H_2O$

b. $C_6H_5\text{-}NHOH \xrightarrow{[O]} C_6H_5\text{-}N{=}O \xrightarrow{NH_2OH} C_6H_5\text{-}N_2OH$

$C_6H_5\text{-}N_2OH \xrightarrow{NH_2OH} [C_6H_5\text{-}\underset{OH}{N}\text{-}N{=}NH] \xrightarrow{-H_2O} 2C_6H_5N_3$

IV. Higher hydronitrogens

A. Saturated (N_nH_{2n+2})

NH_3 - ammonia
N_2H_4 - hydrazine (diamide)
N_3H_5 - triazane (prozane)
N_4H_6 - tetrazane (buzane, hydrotetrazone)

B. Unsaturated hydronitrogens (N_nH_n)

1. $HN{=}NH$ - diimide
   $HN{=}N{=}NH_2$-triazene (diazoamine)
   $H_2N\text{-}N{=}N\text{-}NH_2$ - tetrazene (tetrazone)
   $HN{=}N\text{-}NH\text{-}NH_2$ - isotetrazene (diazohydrazine, buzylene)
   NH_4N_3 - ammonium azide
   $N_2H_5N_3$ - hydrazine azide
2. N_nH_{n-2}
   N_3H - hydrogen azide, hydrazoic acid, azoimide, hydronitric acid, triazoic acid
   N_4H_2 - $HN{=}N\text{-}N{=}NH \longrightarrow$ diiminohydrazine
   N_5H_3 - $HN{=}N\text{-}NH\text{-}N{=}NH \longrightarrow$ bisdiazoamine
   N_6H_4 - $HN{=}N\text{-}NH\text{-}NH\text{-}N{=}NH \longrightarrow$ bisdiazohydrazine
3. N_nH_{n-4}
   N_8H_4 - $HN{=}N\text{-}NH\text{-}N{=}N\text{-}NH\text{-}N{=}NH$ - octazotriene (octazone)

V. General properties of aqueous solutions

VI. Anhydrous HN_3

A. Properties - colorless, extremely explosive liquid boiling at 35.7° and melting at -80° C.

B. Preparation (Dennis and Isham)

VII. Reactions with acids

$HCl \rightarrow NH_4Cl + N_2$
$HBr \rightarrow Br_2 + N_2 + NH_3$
$HI \rightarrow I_2 + N_2 + NH_3$

VIII. Reduction

IX. Metallic azides

A. Two previous methods for NaN_3

B. Insoluble azides

C. Soluble azides

D. In many cases, metallic salts are not obtainable from aqueous solutions as such, but give on standing or evaporation insoluble basic salts of variable composition. Under this classification are Mg, Zn, Yt, La, Ce^{+3}, Cr, Mn, Co, and Ni. With Al, Zr, and Th precipitation of the corresponding hydroxides takes place even in the cold when NaN_3 is added to solutions of salts of these metals in H_2O.

E. Non aqueous media in the preparation of certain azides

F. Double salts

1. $Ni(N_3)_2 \cdot NH_4N_3$ and $Ni(N_3)_2KN_3$ (Co also)
2. Double salts of mercuric cyanide with alkaline hydrazoates and alkaline earth hydrazoates

G. Cobalt complexes containing the azido grouping

1. $[Co(NH_3)_6]\ (N_3)_3$
2. $[Co(NH_3)_5Cl]\ (N_3)_2$
3. $[Co(NH_3)_4(N_3)_2]\ N_3$

Effectiveness of various azides & fulminate

	azide	Fulminate
Cd	1	2
Ag	3	4
Pb	5	
Cu	6	7
Hg^{+}	8	
Hg^{++}		9

H. General properties of metallic azides (see chart)
   1. Photochemical decomposition of azides
   2. Thermal decomposition of azides
   3. Explosive properties of azides

X. Recent uses of azides.

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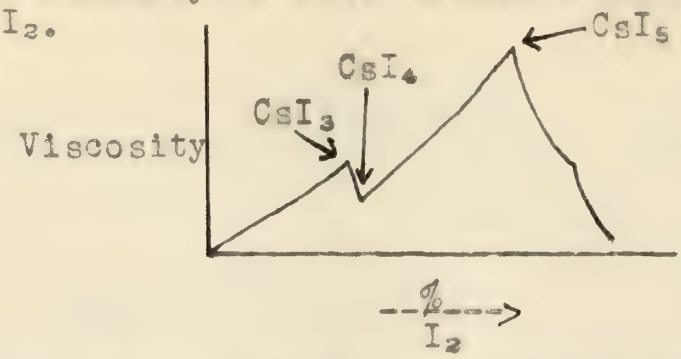
PHYSICAL PROPERTIES OF SOME INORGANIC AZIDES

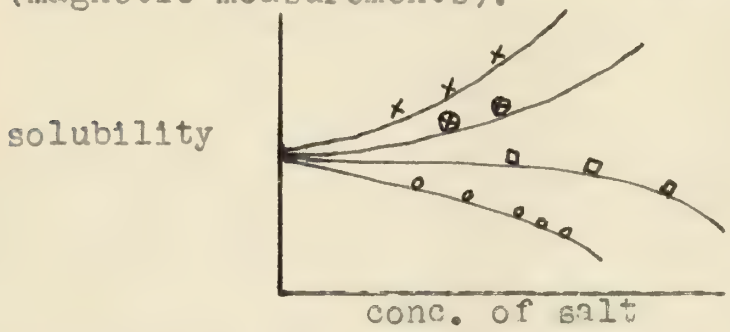
Formula	M.P., °C	Decomp. temp, °C	Decomp. temp. °C	Soly. in 100 g. H_2O	Soly. in other solvents per 100 g. solvent	Crystal form	Other physical properties	Solvates
LiN_3				66.41[16]	C_2H_5OH-20.26[16] insol. in ether			$LiN_3 \cdot H_2O$ $LiN_3 \cdot 2H_2O$ $LiN_3 \cdot 4H_2O$
NaN_3		330 275 300	280	41.7[17]	C_2H_5OH - .22 soluble in liq. NH_3	Hexagonal	$d^{25} = 1.8473$	$NaN_3 \cdot 3H_2O$
KN_3	343 350	355 320	360	49.6[17]	C_2H_5OH- .14[16] sol. in liq. NH_3	Tetragonal	d=2.056	
RbN_3	300 321 330	260 395	310	114.1	Slightly sol. in C_2H_5OH - insol. in ether	Tetragonal	d = 2.9365	
CsN_3	320 326	290 390	350	307.4	C_2H_5OH-1.04[16] insol. in ether	Tetragonal		
NH_4N_3	sublimes 106			13.8^{0}_{26} 20.16_{40} 27.07^{40}	CH_3OH- 3.27^{20}_{20} C_2H_5OH-1.06_{40} 1.33 insol. in ether, C_6H_6. Very sol. in liquid NH_3	Rhombic	$d^{20}_{40} = 1.3459$	$NH_4N_3 \cdot NH_3$ $NH_4N_3 \cdot 5NH_3$
$N(CH_3)_4N_3$		125		very sol.	Sol. CH_3OH- C_2H_5OH. Slightly sol. in C_6H_6- $CHCl_3$ ether	Tetragonal		
$(NH_2OH)_2 \cdot HN_3$	66			very sol.	Sol. in C_2H_5OH insol. in ether			
$N_2H_4 \cdot HN_3$	75.4			very sol.	N_2H_4-190[23] CH_3OH-6.1[23] C_2H_5OH-1.6[23]	Rhombic		$N_2H_5N_3 \cdot N_2H_4$
$Ca(N_3)_2$		110	100		C_2H_5OH- .211	Rhombic		$Ca(N_3)_2 \cdot 2N_2H_4$ $Ca(N_3)_2 \cdot N_2H_4$
$Sr(N_3)_2$		140	110	45.83^{16}_{15}	Slight. C_2H_5OH	Rhombic		
$Ba(N_3)_2$		180	120	16.7	Slight. C_2H_5OH	Rhombic		$Ba(N_3)_2 \cdot H_2O$

See II-A-2-a on page 18.

Measured viscosity of water alcohol solutions of mixtures of CsI and I_2.



CsI_4 has no odd electrons, so must be dimeric. -- Cs_2I_8 (magnetic measurements).



These not exact, but show the right directions.

Solubility of I_2 in aqueous salt solutions (See II, A, 1 on page 18)

- o Na_2SO_4
- × KI
- ⊗ KBr
- □ KCl

See II-B,1. $\frac{[I^-][I_2]}{[I_3^-]}$ = .0014 at 25°. Actually, this is not constant, but falls off with increasing conc. This is due to formation of I_5^-, etc.

NH_4ClIBr. The ion ClIBr is linear with distances 2.38Å and 2.50Å.

In $KICl_4$ the ion ICl_4 is flat and square.

```
Cl   Cl
   I      .
Cl   Cl
```

But what of the extra four extra e^-? Maybe two of them are above and two below the plane of the paper.

THE POLYHALIDES

Mark M. Woyski November 17, 1942

The phenomenon of increased solubility of iodine in alkali iodide solutions was first observed by Gay-Lussac in 1814 and attributed by him to compound formation. Much work and many papers have since been published on the subject of polyhalides but it is only in recent years that any accurate and reliable studies have been made.

I. Crystalline solid polyhalides
   A. Study of binary systems and compounds
      1. Thermal analysis of fusion mixtures
      2. Change of vapor pressure with composition
      3. Conductivity of melts

   B. Ternary systems and compounds
      1. With water as third component
         a) Isothermal equilibria
         b) Thermal analysis
      2. With non-aqueous solvents
         a) Benzene and toluene
         b) Benzonitrile

   C. Results - Tables I and II.

II. Polyhalide ions in solution
   A. Evidence for polyhalide formation
      1. Increase in solubility of halogens
      2. Variation of physical properties with halogen concentration
         a) Viscosity (34)

   B. The equilibria

$$X^- + X_2 = X_3^- = X_5^- \text{ - - - - - - - - - -}$$

      1. By solubility of halogens in halide solutions (10) (11)
      2. By partition of halogen between solution and non-aqueous solvent (10) (21) (27) (28).

III. Structure
   A. Evidence
      1. X-ray diffraction data (26)
      2. Magnetism (24)
      3. Inference

IV. Conclusions
   A. The equilibria $X^- + X_2 = X_3^- = X_5^-$ - - - - - - - - - exist and constants can be found.

$$\frac{[I_2][I^-]}{[I_3^-]} = .00124 \text{ at } 20^\circ \text{ C} \qquad (27)$$

B. Polyhalides consist of an aggregate of halogen molecules around the halide ion

C. The formation of anhydrous crystalline polyhalides is dependent principally upon
   1. The tendency toward formation of polyhalide ion
   2. The relative ionic radii or volumes of cation and anion

D. More complex polyhalides may form if intersticial space is occupied by molecules of a suitable solvent.

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TABLE I

	Binary Systems Metal Iodides-iodine	Ternary Systems with Water A. Iodide, Iodine, Water	B. Other halogen comb.
Li	no compounds	not studied-probably non-existent	$LiICl_4 \cdot 4H_2O$
Na	no compounds NaI ins. in I_2 (3)	$4NaI \cdot 5I_2 \cdot 14H_2O$ (3)(12) $5NaI \cdot 3I_2 \cdot 18H_2O$ or $NaI_2 \cdot 3H_2O$ $2NaI \cdot 3I_2 \cdot 11H_2O$ or $NaI_4 \cdot 2H_2O$	$NaICl_4 \cdot 2H_2O$
K	no compounds KI sol. in I_2 (8)	$KI_3 \cdot H_2O$, $KI_7 \cdot H_2O$ $KI_3 \cdot 2H_2O$ (only) (4)(20)	$KIBr_2 \cdot H_2O$ $2KBr_6 \cdot 3H_2O$ (only) (23)
NH_4	NH_4I_3 (only) (6) other halogen systems not studied	NH_4I_3, $NH_4I_5 \cdot H_2O$ (5) $NH_4I_3 \cdot 3H_2O$ (only)	
Rb	RbI_3 (only) other halogen systems not studied	RbI_3 (only) (2)	
Cs	CsI_3, CsI_4 (only) (7) (30); $CsBr_3$, $CsBr_3$ (inc) (29) other systems not studied	CsI_3, CsI_4 (only) (1) (9)	
Others		BeI_2 forms no solid polyhalides. (31)	$HICl_4 \cdot 4H_2O$; $(CH_3)_4NI_9$, $(C_2H_5)_4NI_7$ (19)

TABLE II

Ternary Systems with Other Solvents

	Benzonitrile (25)	Benzene RX Compounds with I_2 x = I	x = SCN (14)	x = Br (14)
Li	$LiI_3 \cdot 4PhCN$ m.p. 92.5°			
Na	$NaI_3 \cdot 2PhCN$ m.p. 67°	none	none	none
K	$KI_3 \cdot 2PhCN$ m.p. 53°	no binary (18) $KI_9 \cdot 3C_6H_6$ (only)	$KSCN \cdot 6I \cdot 4C_6H_6$	none
NH_4	NH_4I_3	NH_4I_3 (only) (16) no ternary		none
Rb	RbI_3	RbI_3 see also (19) $RbI_7 \cdot 4C_6H_6$ (15) $RbI_8 \cdot 4C_6H_6$ (only)		none
Cs	CsI_3	CsI_3, CsI_4 (17) $CsI_{10} \cdot 2C_6H_6$ (19) or $CsI_9 \cdot 3C_6H_6$ (only)		$CsBrI_2$
Others	$HI_3 \cdot 4PhCN$	Tl_6I_8, TlI_3 FeI_2, AgI, CuI forms no compounds with I_2 (13)		Tl - none

Roll Call

December 1, 1942

Preparation of DCl.

$$\phi COCl + D_2O \longrightarrow \phi COOD + DCl$$

$$\phi COCl + \phi COOD \longrightarrow (\phi CO)_2O + DCl$$

Brown and Groot -- J. Am. Chem. Soc. 64, 2223 (1942).

Preparation of Carbon Black.

Natural Gas + Cl_2 ----> C (30 lbs. per 1000 cubic ft. of natural gas). The usual method of burning natural gas gives 0.5 - 1.0 lbs.

Baumgarten and Bruns. Ber. 74B, 1232-6 (1941).
C.A. 36, 5105

$$2BF_3 + Al_2O_3 \xrightleftharpoons{450^\circ} 2AlF_3 + B_2O_3$$

At higher temps., the reaction goes to left. It goes to right at this temp. because $B_2O_3 + BF_3 \longrightarrow (BOF)_3\uparrow$

$$3SiO_2 + 6BF_3 \xrightarrow{450^\circ} SiF_4\uparrow + (BOF)_3\uparrow$$

$$3TiO_2 + 6BF_3 \xrightarrow{450^\circ} TiF_4\uparrow + (BOF)_3\uparrow$$

This gives a way of extracting Al from silicates.

$$\begin{matrix} MgSiO_3 \\ CaSiO_3 \end{matrix} + BF_3 \longrightarrow \begin{matrix} MgF_2 \\ Ca \end{matrix} + SiF_4 + (BOF)_3\uparrow$$

$$3(Al_2O_3.2SiO_2) + 21BF_3 \longrightarrow \underbrace{6AlF_3}_{\text{This above is left}} + 6SiF_4\uparrow + 7(BOF)_3\uparrow$$

$KAlSi_3O_8$ leaves KF and AlF_3

Ion Conductances.

H^+	-	315	OH^-	-	174
Li^+	-	33	F^-	-	47
Na^+	-	43	Cl^-	-	65
K^+	-	64	Br^-	-	67
Co^+	-	67	I^-	-	66
NH_4^+	-	64	NO_3^-	-	62
Mg^{++}	-	45	$SO_4^=$	-	68
Ba^{++}	-	55			

H^+ and OH^- are abnormally high. This can't be due to small size for Li^+, which is small, has <u>less</u> conductance than Na^+.

INTERATOMIC BONDS AND FORCES; THE HYDROGEN BOND.

W. E. Morrell December 8, 1942.

I. Bonds and Forces:

A. Specific or directed bonds:

1. Electron-pair bonds (as in H_2) — 10–150 kg cal/mole
2. One-electron bonds (H_2^+) — 61 kg cal/mole
3. Three-electron bonds (He_2^+, NO) — 58 " " "

B. Non-specific forces:

1. Ionic forces (NaCl) — 180 kg.cal/mol
2. Attractions between dipoles (Liquid HBr) — maybe 1 kg cal.
3. London forces (Liq. HBr, stronger than preceding) — Dispersion forces.
4. Magnetic forces — ? kg cal.
5. Gravitational forces — 10^{-32} kg. cal. for NaCl; for HBr it is 4 kg cal; for I_2 it is 6.1 kg cal.
6. Repulsive forces
7. Etc. ?

Van der Waals forces

C. Aggregates are formed through combinations of bonds and (or) forces.

1. Electron-pair bonds, ionic forces, London forces, etc., in SO_4^{--}.
2. Ionic and London forces, etc., in NaCl crystal.
3. London and gravitational forces, etc., in I_2 crystal.
4. But no usual combinations of the above account for the abnormal properties of H_2O, HF, and NH_3.

II. Abnormal properties of water:

A. Boiling point
B. Melting point
C. Heat of vaporization
D. Maximum density, and expansion upon cooling
E. Expansion upon freezing
F. Transference numbers of H^+ and OH^-
G. Association

III. HF and NH_3 are similarly abnormal in many respects.

A. Association gives clue.

1. HF_2^- and H_XF_X held together by "Hydrogen Bonds".

IV. The Hydrogen Bond

A. Theories as to structure — H has 4 electrons; resonance, so each H never has more than 2e; purely electrostatic $:\ddot{\underset{..}{F}}:H:\ddot{\underset{..}{F}}:$
B. Stabilities of hydrogen bonds — confined to F, O, N compounds
C. Occurrence

FHF — 6.7 kcal
OHO — 4.5 kcal
NHN — 1.3 kcal

V. Consequences of the existence of the hydrogen bond.

A. The abnormal properties of H_2O, HF, and NH_3 are accounted for.
B. "H_3O^+" and the Bronsted theory.
C. "NH_4OH" and the effect of substitutions in the molecule.

1. P for N
2. S for O
3. HF_2^- for OH^-
4. R for H

D. Consequences in organic chemistry.

Solubilities of acids, alcohols, etc.
Association of acids, alcohols, etc.
Properties of "ortho" compounds.

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THE ALUMS

John C. Bailar, Jr. January 5, 1943

	Li^+ 0.68	Na^+ 0.98	K^+ 1.33	Rb^+ 1.49	Cs^+ 1.67	Ag^+ 1.13	Tl^+ 1.44	NH_4^+ 1.50	$N_2H_4 \cdot H^+$ (10)	$NH_2OH \cdot H^+$ (4)
Al^{+++} 0.55 Colorless	S(8)	S(5) Se	S Se	S Se	S Se	S(7)	S Se	S Se	S	S
Ti^{+++} 0.70 Violet				S	S					
V^{+++} 0.75 (6) Blue or Red		S(6b)	S	S	S		S	S		
Cr^{+++} 0.70 Violet		S Se(2)	S Se	S Se	S		S Se	S Se	S	S
Mn^{+++} Violet			Se	S	S					
Fe^{+++} 0.67 (15) Amythest (Colorless)			S Se	S Se	S Se		S	S		S
Co^{+++} 0.65 Deep Blue or Green			S	S	S		S	S		
Ga^{+++} 0.62 Colorless			S	S	S Se(11)		S	S		
In^{+++} 0.92 Colorless				S	S			S		
Rh^{+++} 0.69 Yellow			S	S	S		S	S		
Ir^{+++} Yellow			S	S	S		S	S		
Tl^{+++} 0.95 Colorless								S(1)		

Other monovalent ions: Cu^+ 0.96, Au^+ 1.37
Other trivalent ions : Sc^{+++} 0.80, Y^{+++} 0.93, La^{+++} 1.15, Pr^{+++} 1.16 .... Lu^{+++} 0.99, Ru^{+++}, Os^{+++}

For organic alums see Topic IIIF.

I. Definition of the term "Alum"

A. Usually defined as the isomorphous series $M'M'''(XO_4)_2 \cdot 12H_2O$
B. Other double sulfates - $NaAl(SO_4)_2 \cdot 11H_2O$; $(NH_4)Al(SO_4)_2 \cdot 4H_2O$ (in which Al can be replaced by rare earths); $(CH_5N_3)_2 \cdot H_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O$ (in which Al can be replaced by Cr, Fe, V) (22).
C. Other isomorphous compounds (14).
$K_2BeF_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and $K_2ZnCl_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

II. Possible Extensions of the Alum Family

A. Other Anions of the XO_4^{--} type -- CrO_4^{--}, MoO_4^{--}, WO_4^{--}, MnO_4^{--}, FeO_4^{--}. The potassium salts of all of these are isomorphous with K_2SO_4 and K_2SeO_4 (13).
B. Other "solvents of crystallization". Hydrogen peroxide (12), ammonia, alcohols, etc.

III. Some Alums of Special Interest

A. Lithium (8)
B. Sodium (5)
C. Silver (7)
D. Separation of Rubidium and Cesium
E. Hydrazine Chromic (10)
F. Organic Alums (9)

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_2H_5NH_2$-Se, $(C_2H_5)_2NH$-Se, $(C_2H_5)_3N$-Se, $C_3H_7NH_2$, -S and Se, $C_5H_{11}NH_2$ (active and optically inactive), $(C_6H_5CH_2)_3N$, C_5H_5N, $(CH_2)_5NH$, coniine (2 propyl piperidine), choline $\left(\begin{matrix} HOCH_2CH_2 \\ (CH_3)_3 \end{matrix}\!\!\diagdown NOH\right)$

G. Titanium
Electrolytic Preparation. Used also for V, Cr, Fe, Co, Mn (21)
Can K^+ and NH_4^+ alums of Ti^{+++} exist?
H. Manganese
Shows the existence of Mn^{+++} ion.
I. Ferric (15)
Color
J. Separation of rhodium and iridium (23)
K. Separation of gallium and indium (16)
L. Thallic (1)

IV. Solubility and Stability Considerations
Stability increases (solubility decreases) as radius of M' increases and as radius of M''' decreases.
Selenic alums more soluble than sulfuric.

V. Crystal Form and Structure

A. Cubic alum crystals (17)
B. X-ray studies (18)

VI. Are Alums Complex Compounds or Double Salts?

A. Minor effect of ionic radii on properties of alums
B. Migration experiments (20)
C. Change of volume on mixing component salts (19)
D. Preparation of $TlAl(SeO_4)_2 \cdot 12H_2O$ from insoluble Tl_2SeO_4.

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Preparation of "Polaroid".

Mellor -- Anstral Chem. Inst. 8, No. 2, page 38 (1940).

$$\left[Co(NH_3)_5Cl\ Cl_2\right] \xrightleftharpoons{H_2SO_4} \left[Co(NH_3)_5Cl\right](HSO_4)_2 \xrightarrow{KI_3} \left[Co(NH_3)_5Cl\right]_4(SO_4)_3(I_3)_2$$

The I_3 ion evidently is the active material. N_3^-, CN_2^-, HF_2^- salts have been prepared and found to have no effect.

Herepathite (a quinine derivative) is also used $(C_2OH_{24}N_2O_2)_4(H_2SO_4)_3(HI_3)_2$.

Crystals are oriented electrically, magnetically, by pairing over a sharp edge, or by drawing from a supersaturated solution.

Urea, K_2PdCl_4 and other substances can be used.

Durham on Hydrates.

$CaCl_2.4H_2O$ exists in 2 forms -- α and β. These, in contact with $CaCl_2.6H_2O$ exert <u>different</u> vapor pressures. <u>Is this isomerism</u>?

$Na_2SO_4.10H_2O$ -- This is lattice H_2O. Very loosely combined. At 32° (or so), anhydrous Na_2SO_4 is formed. $FeCl_3.6H_2O$ -- This is coord. water. On heating to 32.4°, this melts congruently. The H_2O is firmly held.

$Cr_2(SO_4)_3.15H_2O$. All of the H_2O can be removed <u>continuously</u>. Is this a limiting phase (solid soln.) or is this a true compound? If there are actually $15H_2O$ (exactly) it is probably a true compound.

Maybe we have $6H_2O$ for each Cr, and 1 for each $SO_4^{=}$. If so, why does it escape continuously?

$Cr_2(SO_4)_3.18H_2O$ is dehydrated <u>stepwise</u> until only $3H_2O$ are left.

HYDRATES

George S. Durham February 16, 1943

I. Vapor pressure of hydrates

A. Two solid phases necessary to fix pressure

1. Pressure different with different second solid phase

2. Metastable systems possible

B. Solid solutions containing water

II. Classification of hydrates as to behavior upon melting

A. Congruently melting hydrates — melt has same ~~temp~~ composition as the solid

1. Isothermal evaporation of $FeCl_3$ solution

B. Incongruently melting hydrates

1. $Na_2SO_4 \cdot 10H_2O$ — at 32.4° a new solid phase (anhydrous) + a solution appear.

2. Decomposition temperatures

III. Structure of hydrates

A. Werner - coördination; dimeric water

B. Stereochemistry of H_2O also important

C. Classification of hydrates

1. Coördinated H_2O; aquo cations

2. Anion water; hydroxy bonds

3. Lattice water

4. Zeolitic water

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TERMOLECULAR REACTIONS

THE REACTION - $2HNO_3(vapor) + NO \rightarrow 3NO_2 + H_2O$

J. Harold Smith February 23, 1943

I. There are four known third order reactions of the classical kind, such that all of the molecules involved enter into the chemical equation for the reaction. These are the following:

a. $2NO + O_2 \rightarrow 2NO_2$
b. $2NO + Cl_2 \rightleftarrows 2NOCl$
c. $2NO + Br_2 \rightleftarrows 2NOBr$
d. $2NO + H_2 \rightarrow N_2O + H_2O$ (followed by $N_2O + H_2 \rightarrow N_2 + H_2O$)

Each of these is second order with respect to NO and first order with respect to the other reactant. The fact that all termolecular reactions involve two molecules of nitric oxide suggests that possibly there is something unique about the nature of the NO molecule. The transitory existence of a double molecule, $(NO)_2$, has been postulated and used in explaining various aspects of the behavior of the reactions. Another suggestion is that at least somewhat more "inelastic" collisions of longer duration occur between two nitric oxide molecules than is the case with other molecular impacts.

II. The Reaction - $2HNO_3(vapor) + NO \rightarrow 3NO_2 + H_2O$

This termolecular reaction shows behavior very similar to that characteristic of the above-mentioned reactions of nitric oxide. It appears to offer an experimental example of a trimolecular reaction in which nitric oxide, though involved, enters in a first order and not a second order process.

A. Experimental Method.--Since the NO_2 produced by the reaction is the only colored substance involved, the reaction is easily followed by a colorimetric method. The large amount of NO_2 formed by the reaction makes this method particularly advantageous. Light intensities are measured using a sensitive photronic cell and a micro-ammeter for measuring the current.

B. Experimental Results

1. Stoichiometry - the reaction is as represented by the equation:

$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O$$

Under the conditions used it is complete as written, and essentially free from side reactions

2. Order
   a. NO - first order behavior
   b. HNO_3 - apparently second order, although additional data must be obtained before it can be decided that it may not be somewhere between first and second order.
3. Homogeneity - quantitative data as yet not available, but qualitative observations in vessels of widely different surface-volume ratio indicate that the reaction is essentially a homogeneous gas phase reaction.
4. Temperature behavior - the rate decreases sharply as the temperature is raised from 0 to 25° C. This decrease continues, though less rapidly, until a temperature of 40-45° is reached. Above 45° more normal behavior is observed, with a slight increase in rate as the temperature is raised (at least to 90° C.)

III. Discussion of the temperature behavior

A. Ordinary Bimolecular Processes.--For most reactions the rate doubles or trebles as the temperature is raised 10°. The explanation of this lies largely in the fact that the number of molecules with high energies (i.e. equal to or greater than the required energy of activation) increases much more rapidly with an increase in temperature than does the average energy. Since the rate depends primarily upon the number of collisions involving activated molecules, a fairly high positive temperature coefficient is normally to be expected.

B. Termolecular Reactions.--In terms of the collision theory, the rate of a termolecular reaction will be determined, similarly, by the number of triple collisions between molecules sufficiently activated that a reaction can occur. For a perfect gas, both the number of triple collisions and the energy available for activation increase with temperature. In such a case a positive temperature coefficient is to be expected. In order to account for an observed negative coefficient it is assumed that the reactants involved are not perfect gases, and that either "inelastic" triple collisions are involved or else double molecules have at least a transitory existence. In this way, an increase in the temperature may, in effect, decrease the number of "inelastic" triple collisions. This factor would tend to decrease the rate. Opposed to this would be the higher efficiency for reaction at the higher temperature, due to the availability of energy for activation. It is possible that the two factors may be of such magnitude that under appropriate conditions the rate of a termolecular reaction may increase, decrease, or show practically no change with temperature.

It is found experimentally that the $NO + O_2$ reaction has a slight negative temperature coefficient throughout the entire range studied. The reactions of NO with Cl_2 and Br_2 depend only slightly upon temperature, and the $NO + H_2$ reaction has a high positive temperature coefficient. The temperature behavior of the $HNO_3 + NO$ reaction has been described.

Eyring has approached the problem on the basis of the theory of absolute reaction rates using the methods of statistical mechanics in an attempt to explain the behavior of the termolecular reactions involving nitric oxide.

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(The above contain numerous references to the original literature)

THE HALIDES AND OXYHALIDES OF SELENIUM

J. Arthur Mattern March 2, 1943

A. Compounds reported for sulfur, selenium and tellurium (see table)
B. The monohalides Se_2Cl_2, Se_2Br_2 and (Se_2I_2)
   1. Se_2Cl_2
      (a) Preparation
         (1) $2Se + Cl_2 \longrightarrow Se_2Cl_2$ (Berzelius, 1818)
         (2) $SeO_2 + 4HCl + 3Se \xrightarrow{H_2SO_4} 2Se_2Cl_2 + 2H_2O$
         (3) $2SeO_2 + 2HCl + 3SO_2 \longrightarrow Se_2Cl_2 + 2SO_3 + H_2SO_4$
         (4) $3Se + SeOCl_2 + 4HCl \longrightarrow 2Se_2Cl_2 + 2H_2O$
      (b) Physical properties
      (c) Chemical properties
         (1) Decomposition $2Se_2Cl_2 \rightleftharpoons SeCl_4 + 3Se$
         (2) Hydrolysis $2Se_2Cl_2 + 2H_2O \longrightarrow SeO_2 + 3Se + 4HCl$
         (3) Action as a chlorinating agent
            $2P + 3Se_2Cl_2 \longrightarrow 2PCl_3 + 6Se$
            $NH_3 + 2Se_2Cl_2 \longrightarrow Se_2NCl + 2Se + 3HCl$ (+ trace of SeN)
         (4) $S_2Cl_2 \xrightarrow{Se} Se_2Cl_2 \xrightarrow{Te} Te_2Cl_2$
         (5) $C_2H_4 + Se_2Cl_2 \longrightarrow (ClC_2H_4)_2Se + Se$
            $(ClC_2H_4)_2Se + Se_2Cl_2 \longrightarrow (ClC_2H_4)_2SeCl_2 + 2Se$
   2. Se_2Br_2
      (a) Preparation
      (b) Properties - Comparison with Se_2Cl_2
         $4NH_3 + 7Se_2Br_2 \longrightarrow 2Se_2N_2Br + 10Se + 12HBr$
         $2PhMgBr + Se_2Br_2 \longrightarrow 2MgBr_2 + (PhSe)_2$ (also $\phi Se \phi$ and $\phi \overset{Br_2}{Se} \phi$)
   3. The existence of Se_2I_2 or other iodides of selenium
   4. Structure of the monohalides
      (a) Two possible structures: (1) $SeSeX_2$ (2) XSeSeX
      (b) Evidences for (1)
      (c) Evidences for (2)

C. The dihalides ($SeCl_2$) and ($SeBr_2$)
   1. Evidence for their existence
   2. Evidence casting doubt upon their existence

D. The tetrahalides SeF_4, $SeCl_4$, $SeBr_4$ and mixed halides
   1. SeF_4
      (a) Preparation $4AgF + SeCl_4 \longrightarrow SeF_4 + 4AgCl$ (Prideaux, 1927)
      (b) Physical properties
      (c) Reactions
         (1) Attacks glass $SeF_4 + SiO_2 \longrightarrow SeO_2 + SiF_4$
         (2) Hydrolysis $SeF_4 + 3H_2O \longrightarrow 4HF + H_2SeO_3$
         (3) $4P + 3SeF_4 \longrightarrow 4PF_3 + 3Se$
   2. $SeCl_4$
      (a) Preparation
         (1) $Se + 2Cl_2 \longrightarrow SeCl_4$
         (2) $\left.\begin{matrix} PCl_5 \\ HCl \\ SOCl_2 \end{matrix}\right\} + SeO_2 \longrightarrow SeCl_4 + \left\{\begin{matrix} POCl_3 \\ H_2O \\ SO_2 \end{matrix}\right.$
         (3) $Na_2SeO_4 + 4H_2SO_4 + 6NaCl \longrightarrow SeCl_4 + Cl_2 + 4Na_2SO_4 + 4H_2O$
         (4) $H_2SeO_4 + 6CH_3COCl \longrightarrow SeCl_4 + Cl_2 + 3(CH_3CO)_2O + H_2O$
      (b) Physical properties
      (c) Reactions
         (1) Decomposition $2SeCl_4 \longrightarrow Se_2Cl_2 + 3Cl_2$
            $SeCl_4 \longrightarrow SeCl_2 + Cl_2$

(2) Hydrolysis $SeCl_4 + H_2O \rightarrow SeOCl_2 + 2HCl$
$SeCl_4 + 2H_2O \rightarrow SeO_2 + 4HCl$
(3) $3Cu + 2SeCl_4 \rightarrow 3CuCl_2 + Se_2Cl_2$
$Se_2Cl_2 + 5Cu \rightarrow 2Cu_2Se + CuCl_2$
(4) $NH_3 + 3SeCl_4 \rightarrow 12NH_4Cl + N_4S_3$
(5) Reactions with organic reagents

3. $SeBr_4$
(a) Preparation
(b) Properties and reactions - comparison with $SeCl_4$
(1) $3SeBr_4 + 16NH_3 \rightarrow 2SeN + Se + N_2 + 12NH_4Br$
(2) Bromoselenates
(a) Formation $2KBr + SeBr_4 \rightarrow K_2SeBr_6$
$Br_2 + Se + HBr \rightarrow H_2Se\ Br_6$
(b) Action with water

4. Mixed tetrahalides $SeCl_3Br$, $SeCl_2Br_2$, $SeClBr_3$
(a) Preparation $Se_2Br_2 + 3Cl_2 \rightarrow 2SeCl_3Br$
$Se_2Cl_2 + 3Br_2 \rightarrow 2SeClBr_3$
$SeBr_4 + Se_2Br_2 + 3Cl_2 \rightarrow 3SeCl_2Br_2$

E. The hexahalides SeF_6
1. Preparation $Se + 3F_2 \rightarrow SeF_6$
2. Properties
3. Reactions
(a) $SeF_6 + 2NH_3 \rightarrow Se + 6HF + N_2$
4. Structure

F. The oxyhalides $SeOF_2$, $SeOCl_2$, $SeOBr_2$
1. $SeOF_2$
(a) Preparation
(1) $2AgF + SeOCl_2 \rightarrow SeOF_2 + 2AgCl$
(2) $SeO_2 + 2HF \rightleftharpoons SeOF_2 + H_2O$
(b) Properties
(c) Reactions
(1) With phosphorus $4P + 6SeOF_2 \rightarrow 4POF_3 + SeO_2 + 5Se$
$4P + 6SeOF_2 \rightarrow 4PF_3 + 3SeO_2 + 3Se$
(2) With silica $2SeOF_2 + SiO_2 \rightarrow SiF_4 + 2SeO_2$

2. $SeOCl_2$
(a) Preparation
(1) $SeO_2 + SeCl_4 \rightarrow 2SeOCl_2$ (in $CHCl_3$ or CCl_4)
(2) $SeCl_4 + H_2O \rightarrow SeOCl_2 + 2HCl$
(3) $SeO_2 + 2HCl \rightarrow SeO_2.2HCl \xrightarrow{-H_2O} SeOCl_2$
(4) $2SeO_2 + 2NaCl \rightarrow SeOCl_2 + Na_2SeO_3$ (1889)
(b) Physical properties
(c) Chemical properties - behavior as an oxidizing acid chloride
(1) Action on metals $3Cu + 4SeOCl_2 \rightarrow 3CuCl_2 + 2SeO_2 + Se_2Cl_2$
(2) Action on oxides, carbonates and sulfides
$CuO + SeOCl_2 \rightarrow CuCl_2 + SeO_2$
(3) Action on olefins $2C_nH_{2n} + SeOCl_2 \rightarrow (ClC_nH_{2n})_2SeCl_2 + SeO_2$
(4) Action on pyridine and quinoline
$Py + SeOCl_2 \rightarrow PySeOCl_2$ and Py_2SeOCl_2
(5) Action on proteins, rubber, gums, resins, paints, asphalts, etc.
(6) Action on $BaSO_4$ - $SeOCl_2$ replaces $BaSO_4$.
(d) $SeOCl_2$ as a parent solvent
(1) Ionization $2SeOCl_2 \rightleftharpoons (SeOCl \cdot SeOCl_2)^+ + Cl^-$
(2) Behavior upon electrolysis
(a) Cathode $6(SeOCl \cdot SeOCl_2)^+ + 6e^- \rightarrow 2SeO_2 + Se_2Cl_2 + 8SeOCl_2$
(b) Anode $2Cl^- \rightarrow Cl_2 + 2e^-$

(3) Acid-base studies by conductance titrations

base $Py + SeOCl_2 \rightleftharpoons PySeOCl_2 \rightleftharpoons PySeOCl^+ + Cl^-$

acid $SO_3 + SeOCl_2 \rightleftharpoons SO_3SeOCl_2 \rightleftharpoons SO_3Cl^- + SeOCl^+$

neutralization $PySeOCl_2 + SO_3SeOCl_2 \rightleftharpoons (PySeOCl)SO_3Cl + SeOCl_2$

3. $SeOBr_2$
   (a) Preparation $Se + SeO_2 + 2Br_2 \longrightarrow 2SeOBr_2$
   (b) Properties - comparison with $SeOCl_2$

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The halides and oxyhalides of sulfur, selenium and tellurium

	F	Cl	Br	I
		S_4Cl_2		
		S_3Cl_2		
Monohalides	S_2F_2	S_2Cl_2 Se_2Cl_2	S_2Br_2 Se_2Br_2	Se_2I_2(?)
Dihalides	SF_2	SCl_2 $SeCl_2$(?) $TeCl_2$	SBr_2(?) $SeBr_2$(?) $TeBr_2$	TeI_2
Tetrahalides	SF_4 SeF_4 TeF_4	SCl_4 $SeCl_4$ $TeCl_4$	SBr_4(?) $SeBr_4$ $TeBr_4$	TeI_4
Hexahalides	SF_6 SeF_6 TeF_6			
Oxyhalides	SOF_2 $SeOF_2$ $2TeOF_2 \cdot H_2O$	$SOCl_2$ $SeOCl_2$	$SOBr_2$ $SeOBr_2$ $TeOBr_2$	
	$2TeF_4 \cdot 3TeO_2$		$TeOCl_2$	
	SO_2F_2	SO_2Cl_2		
		$S_2O_3Cl_4$		
	S_2F_{10}	$S_2O_5Cl_2$		

Alloys can be plated out by complexing, etc. until the reduction potentials are comparable, thus:

	E_o volts	1 M $MeSO_4$	+.2 M KCN	+.4 M KCN	+1 M KCN
Cu	+ .34	+ .31	- .61	- .96	-1.17
Zn	+ .76	- .79	-1.03	-1.18	-1.23
Cd	- .40	- .44	-. 71	- .87	-.90

COMPLEX IONS IN THE ELECTRODEPOSITION OF METALS

M. G. Herda March 23, 1943

INTRODUCTION: (Extracts from Modern Electroplating 1942)

CONSTITUTION OF SOLUTIONS: "In spite of great progress in the study of dilute solutions, illustrated by the development and extension of the Debye-Hückel theory, there is still no adequate theory of the constitution of the concentrated solutions (frequently from 1 to 4 M) that are commonly used in commercial plating."

MECHANISM OF DEPOSITION: "In spite of the fact that cyanide plating baths have been extensively used for about 100 years, their constitution is not well established, and there is no general agreement regarding the mechanism of metal deposition from solutions."

ADDITION AGENTS: (Colloidal and crystalloidal organic compounds): "The present inability to throw light on this and related questions is well illustrated by a recent survey of the effects of over 100 organic compounds upon the brightness of nickel deposits, by E. Raub and M. Wittum. No definite, simple relations were found on brightness or polarization."

PURPOSE OF COORDINATION (OR COMPLEXING) IONS:

1. To prevent displacement deposition of noble metals on baser metals - e.g., $Cu^{++} + Zn \rightarrow Zn^{++} + Cu$.
   A spongy Cu deposit results making an adherent electrolytic deposit impossible. Not so with $Cu(CN)_2^-$

2. To obtain a fine crystalline deposit capable of taking a polish.
   Ag, Pb, and many others form coarse granular deposits unless complexed.

3. To improve throwing power.
   If cation is present mainly as complex ions, even covering over uneven surfaces results.
   Zn^{++} = very poor throwing power
   $Zn(CN)_4^=$ very good throwing power

4. To allow co-deposition of metals, i.e., electrolytic formation of alloys.
   (a) Almost any desirable alloy can be formed by selecting the proper complexing ions for the various components.
   (b) Even metals which do not plate out alone will plate out in alloys, e.g., Mo.

ALLOYS: If the reduction potential of metallic ions can be made to assume comparable values, co-deposition takes place.

	Cathode potential in volts			
current density	N $CuSO_4$	.1N $Cu(CN)_2^-$	N $ZnSO_4$	.1N $Zn(CN)_4^=$
.0 (equilibrium)	+.302	-.610	-.795	-1.033
.001 amp/cm^2	+.273	-.77	-.829	-1.12
.003 amp/cm^2	+.262	-1.12	-.838	-1.25

To carry this to an extreme, Zn can be plated out in preference to Cu.

CONTROL: If the cations are held in different complexes their "free" concentration in solution can be controlled thus controlling the composition of the alloy.

ALLOYS:

Cu-Sn	(Cu as cyanide, Sn as stannate)
Ag-Pb	(Ag as cyanide, Pb as tartrate)
Cu-Zn	(All three as cyanide, but recent conductivity and
Cd-Zn	(pH data show that if NaOH is added, 75-90% of the
Cu-Cd-Zn	(zinc is present as the zincate)

OTHER ALLOYS: Decorative: Ni-Co, Ni-Zn, Ni-Cd, Zn-Mo, Ni-Mo, etc.
Protective: Cd-Zn, W-Ni, Pb-Bi, etc.
Bearing metals: Ag-Pb, Ag-Cd, Pb-Sn, etc.

COMPILED LIST OF COMPLEXING IONS AND MOLECULES IN USE:

The iron group (Fe, Co, Ni, Cu, Zn) can all be plated out of an acid-sulfate bath.

Zn - Sulfate, cyanide
Cr - Sulfate, fluoride, fluosilicate
Co - Sulfate, triethanolamine, sulfamate
Cu (basic bath) - $Cu(CN)_3^{=}$, $Cu(CN)_2^{-}$, $Cu(CN)_4^{\equiv}$
Cu (acidic bath) - Sulfate, oxalate, pyrophosphate
Cd - Cyanide
Au - Ferrocyanide, pyrophosphate, $Au(CN)_2^{-}$, $AuCl_4^{-}$
Pb (acidic) - fluosilicate, nitrate, acetate, fluoborate, perchlorate, oxalate, dithionate, sulfamate
(basic) - plumbate, cyanide
Pt - $PtCl_6^{=}$, nitrate, nitrite
Pd - $PdCl_4^{=}$, ammino palladium complex
Rh - sulfate, phosphate
Ag - Cyanide, ferrocyanide, iodide, nitrate, sulfate, fluoborate, fluoride
Sn - Stannate, chloride, tartrates, cyanide, thiosulfate
W - Alkaline tungstate
Mo - Pyrophosphate, tartrate, citrate, lactate (requires a carrier such as Fe or Ni)
In - Sulfate
As - Cyanide, pyrophosphate, arsenate
Sb - from Schlippe's salt bath.

Zialite bath for Ni is patented (1933?). It is a basic bath containing citrate, NH_4OH, etc.

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THE ATOMIC STRUCTURE OF MONTMORILLONITE AND KAOLINITE CLAYS AS RELATED TO THEIR CHEMICAL AND PHYSICAL BEHAVIOUR

R. W. Parry

March 30, 1943

I. Importance and Properties
   A. Important in agriculture as chief constituent of soil colloids; used in engineering, ceramics, rubber industry, etc.
   B. Typical of two different groups of clay minerals
      1. Montmorillonite group - highly hydrated, high adsorptive properties, definite basal cleavage
      2. Kaolinite group - low hydration, adsorptive properties, and less definite basal cleavage

II. Structure of Minerals
   A. Historical (3)(4)(5)(7) etc.
   B. Primary structural units (1)
      1. Alumina or aluminum hydroxide sheet - 2 sheets of closely packed oxygens or hydroxyls between which Al atoms are imbedded in such a position that they are equidistant from six oxygens or hydroxyls
      2. Silica sheet - Sheet of loosely packed oxygen atoms with each oxygen linked to two Si atoms directly beneath. The Si atoms are in tetrahedral positions, three valences being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an oxygen atom.
   C. Structure of Montmorillonite (2:1 lattice)
      1. Structure of Hoffman, Endell, and Wilm (5)
         a. Formula $(OH)_4Al_4Si_8O_{20} \cdot nH_2O$
         b. One alumina sheet between two silica sheets
            Diagram - Ref. (1) page 239
         c. Expanding lattice
         d. Replacement of Al^{+++} by Mg^{++} or Fe^{+++}
         e. Replacement of Si^{++++} by Al^{+++}; extensive replacements yield non expanding lattice (6)
      2. Structure of Edelman and Favejee (7)
         a. Formula $(OH)_{12}Al_4Si_8O_{16} \cdot nH_2O$
         b. Structure - Diagram Ref. (1) page 242
         c. Superior in explaining base exchange
   D. Structure of Kaolinite (1:1 lattice)
      1. One alumina and one silica sheet
      2. Structural diagram ref. (1) page 246
      3. Non expanding lattice
         a. Hydrogen bonding
      4. Cleavage
      5. No substitution for Al^{+++} or Si^{++++}

III. Base Exchange and Structure
   A. Montmorillonite 60-100 m.e./100 gms. clay (1)
      Kaolinite 3- 15 m.e./100 gms. "

B. Cause of adsorptive properties of clay minerals
   1. Montmorillonite
      a. 80% exchange positions on basal plane surfaces (8)
      b. Exchange positions on basal plane and structure of Hoffman, et.al.
      c. Exchange positions on basal plane and structure of Edelman and Favejee; H^+ substitution
      d. Exchange positions on edges
   2. Kaolinite
      a. No exchange positions between sheets
      b. Capacity from broken O bonds and replaceable H^+ exposed on edges (1)
      c. Kaolinite shows exchange capacity for certain anions as phosphate, etc. (1)
         1. Replacement of H^+ to give distorted lattice
C. Relation of Particle size to exchange capacity (9)(10)(11)
   1. Montmorillonite - independent of size
   2. Kaolinite - increases with decreasing size

IV. The Clay Water System
   A. Older theory - oriented dipoles (14)
   B. Theory of Hendricks and Jefferson (15)
      1. Hexagonal network on basal planes
         a. Hydrates (16)
      2. Bridged to oxygens of silica by H-bridge
      3. Double bridging from H of mineral to O of water
      4. Relation to kaolinite and montmorillonite
   C. Broken bond water
   D. Forces binding planar water of kaolinite on outer edges unexplained.

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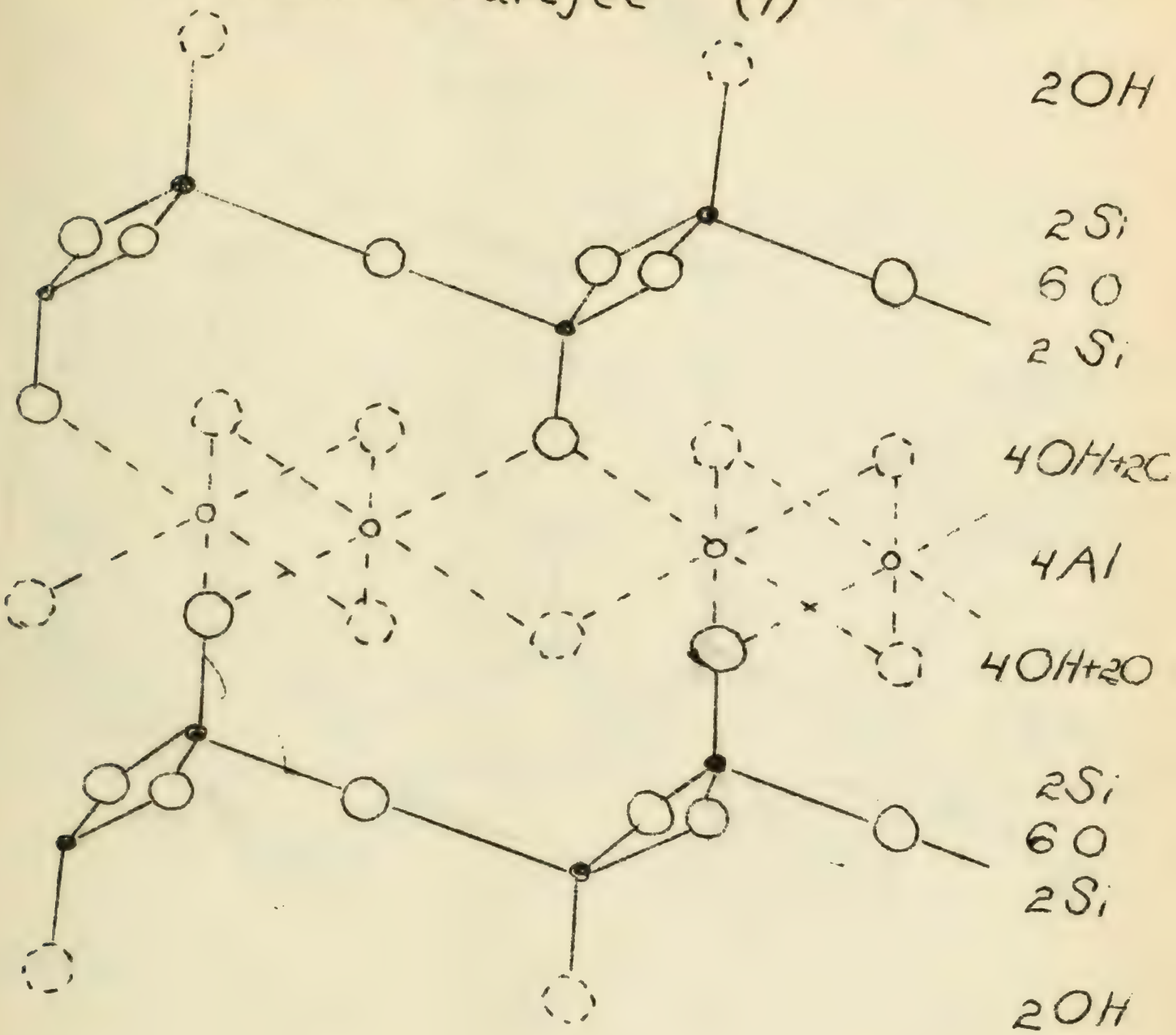
Montmorillonite $(OH)_2Al_4Si_8O_{16} \cdot nH_2O$
Edelman & Favejee (7)

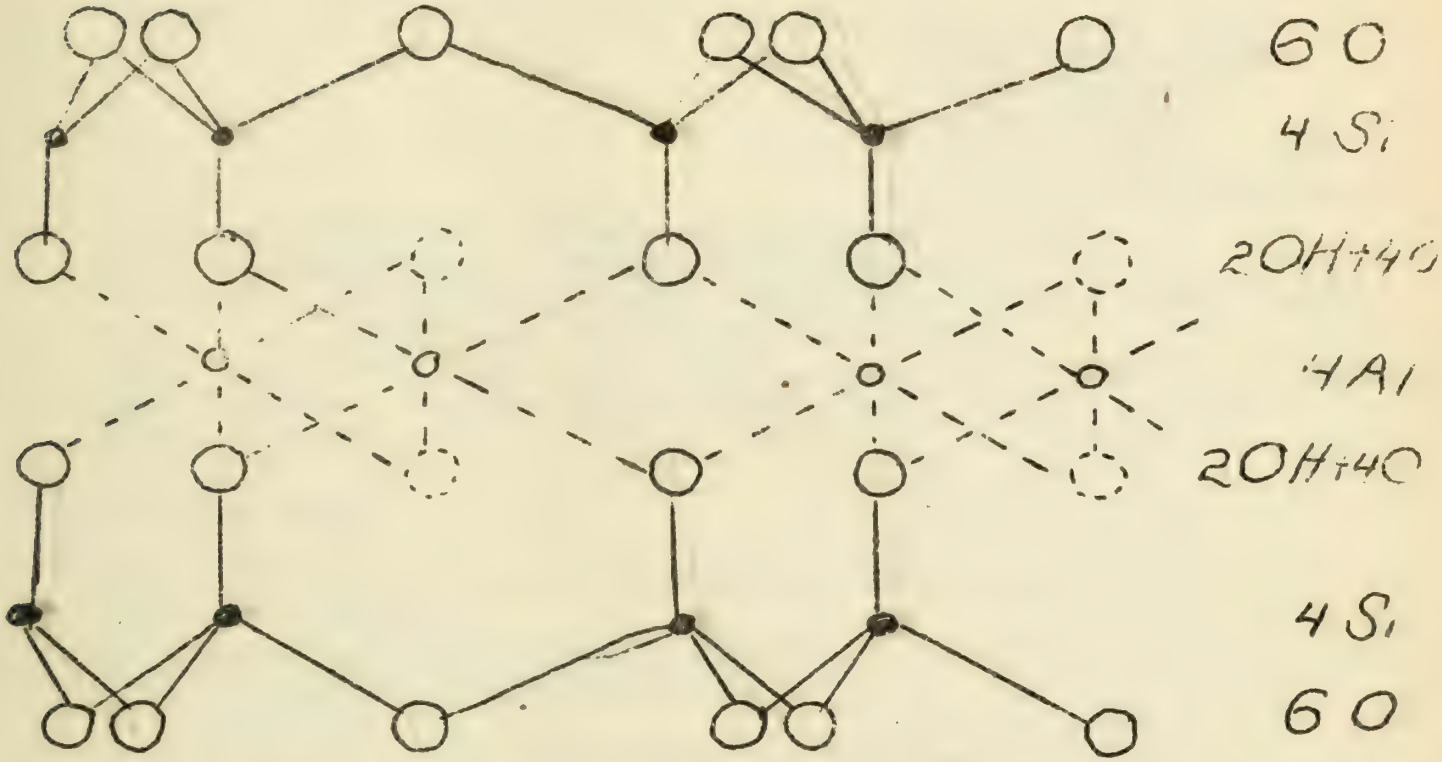


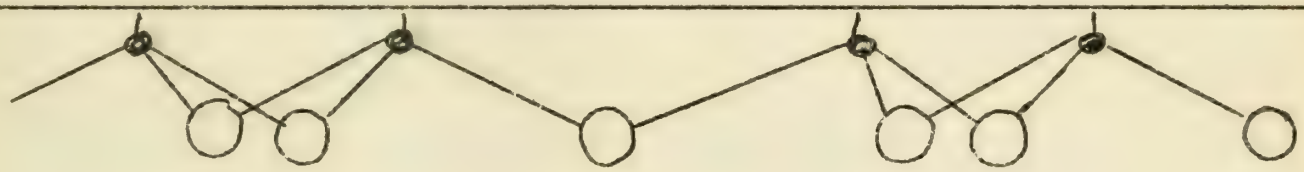
OH = ○ Si = ● O = O Al = o

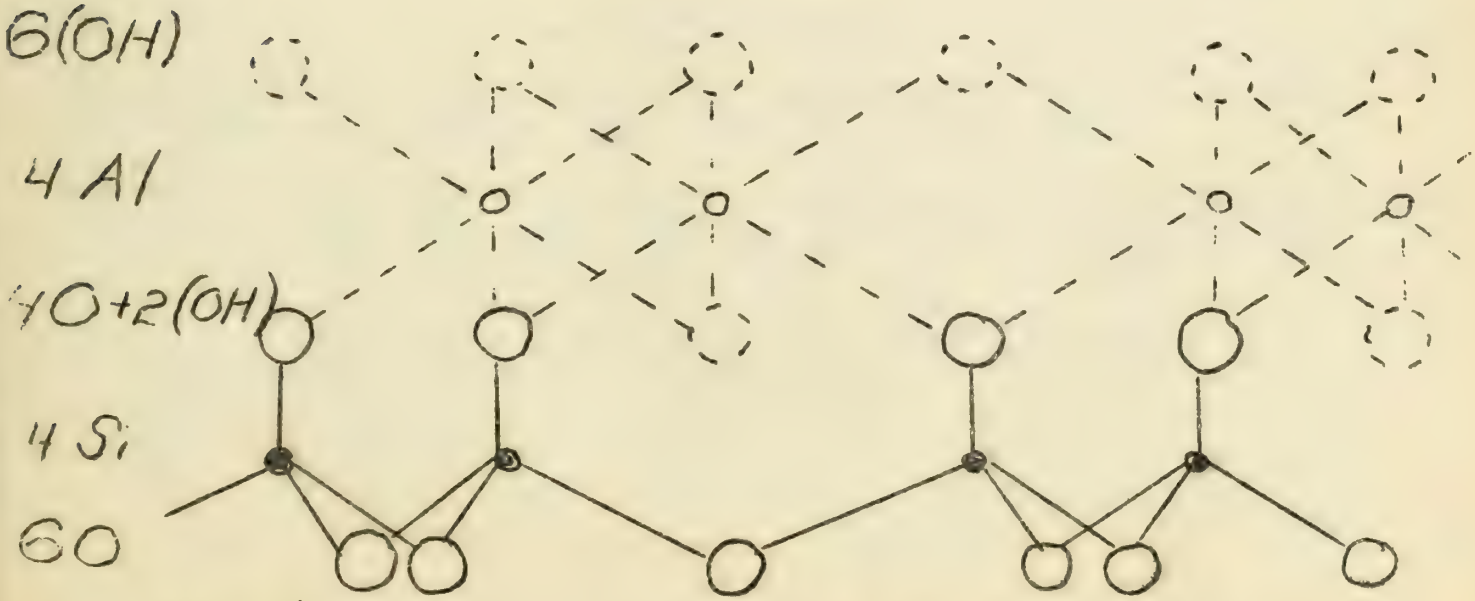
Montmorillonite $(OH)_4 Al_4 Si_8 O_{20} \cdot nH_2O$

Hoffman, Endel & Wilm (5)

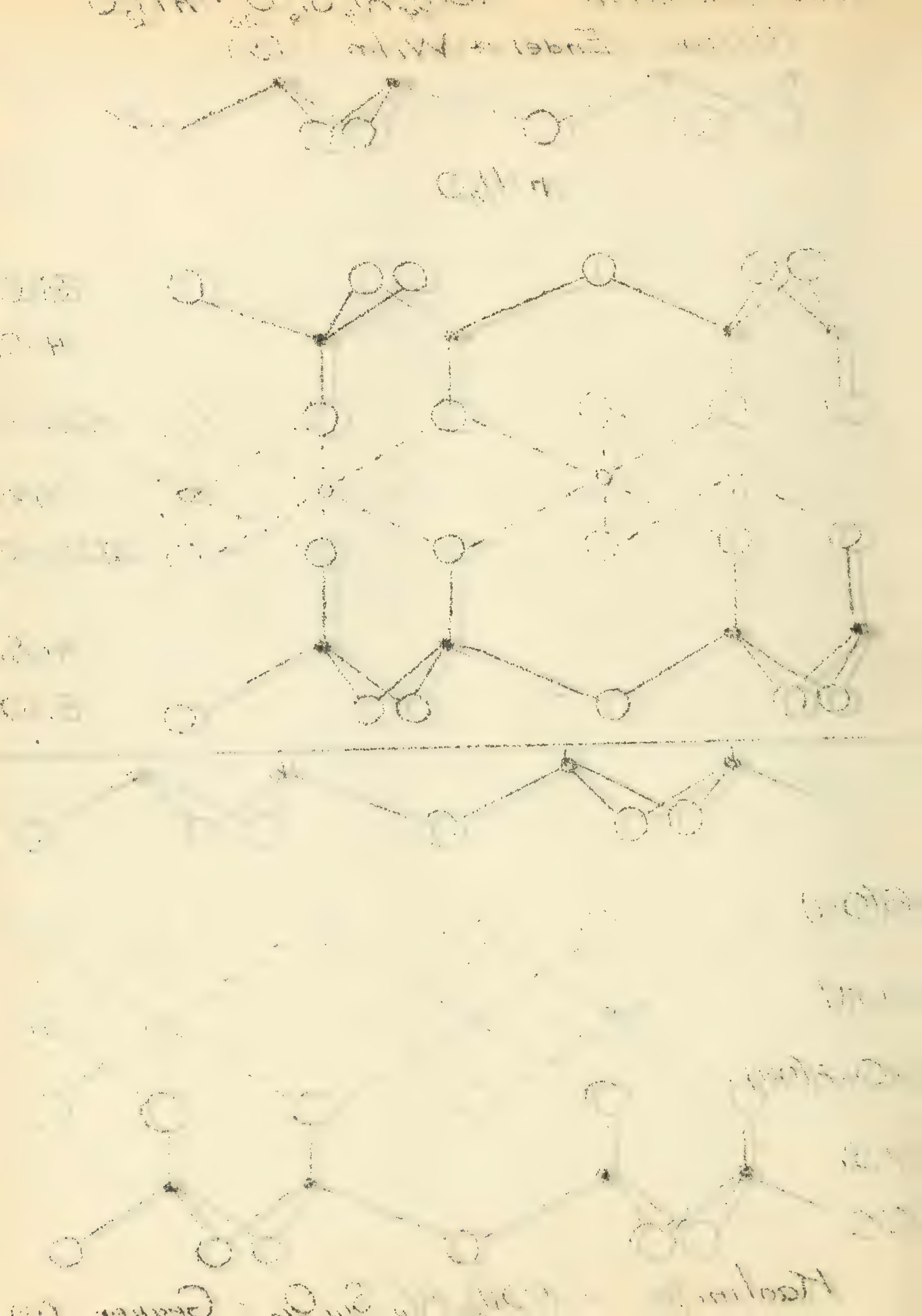
$n\ H_2O$







Kaolinite - $(OH)_8 Al_4 Si_4 O_{10}$ - Gruner (18)



200TH ANNIVERSARY OF KLAPROTH AND LAVOISIER

Virginia Bartow April 6, 1943

Martin Heinrich Klaproth - December 1, 1743 - January 1, 1817

I. Life

Born Wernigorode
Educated - State School
Training - Apothecary's apprentice - 1759-64 Home town
1764-66 Quedlinburg
1766-68 Hanover
1768-70 Berlin
1770 Danzig
1771 Berlin with Rose
1783 (Approximate) - Bought Flemming Laboratory
1810 - Bought room of academical chemists
Lecturer - Artillery Academy, Royal War School, Royal Mining Institute, University of Berlin
1787 Royal Academy of Arts, 1788 Royal Berlin Academy of Science
1811 Order of the Red Eagle - III Class
Died in Berlin

II. Civil Servant

III. Scientific Achievements - Analytical Chemistry

Improved Analyses
Discoverer of new earths or elements: U, Zr, Ti, Sr, Te, Ce
Confirmation of discoveries Be, Y
New Apparatus
Publications - Collected works in 6 volumes
207 articles
Editor
Translator
Miscellaneous
Champion of the "New Theory" of Lavoisier

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* 1939

Antoine Laurent Lavoisier - August 26, 1743 - May 8, 1794

I. Life
- Born Paris
- Education - College Mazarin, Jardin des Plantes - travel
- Marriage - Marie Anne Pierette Paulze 1771
- Died Paris

II. Scientific Work
- Scientific outlook in 1770 - Phlogiston Period and Pneumatic Chemistry
- Early work and recognition
  - a) Barometers
  - b) Water analysis
  - c) Gypsum
  - d) Street lighting
  - e) Adjoint member of the Academy of Sciences 1768
    - 1. Duties
    - 2. Secretary
- Important Research Problems
  - a) Conversion of water to earth - Contrast Scheele
  - b) The nature of water - Contrast Cavendish
  - c) Exp. steam and hot iron
  - d) Combustion and calcination
    - 1. Diamond
    - 2. Sulfur and phosphorus
    - 3. Lead and tin
  - e) The nature of the active principle of the air - Contrast Priestley
  - f) Respiration
- The "New Theory"
- Nomenclature
- "Traite Elementaire de Chimie"
  - a) Table of elements
  - b) Equations
  - c) Caloric
  - d) Oxygen theory of acids
- Annales de Chimie
- Financier-Member Ferme Generale - secretary
- State Official - Member of the Regie des Poudres - secretary
  - La Societe et le Comite d'agriculture
  - Representative from Blois
  - The 89 Club
  - The Committee of Weights and Measures
- Reformer
  - Taxes - Agriculture - Prisons - Banking - Coinage - Metric System - Mesmer
- Arrest - Charges - Trial and Execution
- Honorary Funeral 1795
- Influence in America

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Grimaux, E., "Lavoisier", Bailliere and Co., Paris, 1888, 398 pp.

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McKie, D., "Antoine Lavoisier", Lippincott Co., Philadelphia, 303 pp.

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$[Co(NH_3)_6]F_3$ crystallizes with 3 HF or 6 HF, depending on HF concentration.

Many oxides add HF --- SO_3 gives HSO_3F

acids, too $H_3BO_3 + HF \rightarrow H\left[\begin{matrix} H-O \\ H-O \end{matrix}\!>B<\!\begin{matrix} F \\ F \end{matrix}\right]$

CaF_2 is

COORDINATION COMPOUNDS OF FLUORINE

Mark M. Woyski

April 27, 1943

I. General and Theoretical

A. Complex formation with hydrogen fluoride

$$M^nF_n + xHF \longrightarrow M^nF_n \cdot xHF$$

where M represents any of a great majority of the elements; N, its valence; x, an integer (or integers) characteristic of M.

B. The nature of these complexes
1. Hydrogen bonded structures
2. True coordination compounds $[M^nF_x]^{-(x-n)}$
3. Indefinite or unknown structures

C. The relative stability of halide complexes
1. As a function of ionization potential, polarizability and ionic sizes
2. Energy considerations; thermochemical data

D. Properties
1. General
2. A unique type of isomorphism

$[BeF_4]^{=}$ and $[SO_4]^{=}$

$[BF_4]^{-}$, $[SO_3F]^{-}$ and $[ClO_4]^{-}$

II. Fluorine Coordination Compounds of Individual Elements

Element	Types	Remarks
Group I		
Alkali Metals	$MF \cdot xHF$ x = 1,2 or 3	hydrogen bonded structures HF_2^- ion exists in solution
Cu, Ag, Au	various double salts AgF·3HF easily breaks down to AgF·HF which is stable.	insufficient evidence of structure; evidence of complex ions in solution, i.e. CuF_2, insol. in H_2O dissolves in HF aq.
Group II		
Alkaline earth metals	$MF_2 \cdot xHF$ various double salts	hydrogen bonded structures no evidence of complex metal ion in solution
Zn, Cd, Hg	various double salts	structure unknown
Be	$[BeF_4]^{=}$	stable complex; F not precipitated by Pb^{+2}
Group III		
B	$[BF_4]^{-}$	stable complex, hydrolyzes very slightly
Al, Sc, Ga, In	$[M^{+3}F_6]^{\equiv}$ also $[Al(H_2O)F_5]^{=}$	stability decreases with increasing atomic wt. and electropositivity of M
Y, Ce^{+3}, Tl^{+3}		CeF_3 is insoluble in HF aq.
Ce^{+4}	no information $[Ce^{+4}F_6]^{=}$	unstable in solution; liberates $O_2 \longrightarrow CeF_3 \downarrow$

Element	Types	Remarks
Group IV		
All M^{+4}	$[M^{+4}F_6]^{=}$	stability toward hydrolysis decreases with atomic wt. Pb^{+2} does not precipitate F
Zr^{+4}, Ti^{+4}	$[M^{+4}F_7]^{\equiv}$	form complexes of Si, Ti, Zr, Ge, Sn very unstable; crystallize from solns. of high F^- concn.
Group V		
N^{+5}	? $[NF_6]^-$; $[NOF_3]^{=}$	The existence of these is disputed
P^{+5}	$[PO_3F]^{=}$; $[PO_2F_2]^-$; $[PF_6]^-$	equilibrium in soln. depends on F^- concn. Hydrolyze only slowly when isolated
As^{+5}, Sb^{+5}	$[M^{+5}F_6]^-$	hydrolyze readily
V^{+5}	oxyfluovanadates $[VO_2F_4]^{\equiv}$ and others	type depends on acid and fluoride ion concentrations
Cb^{+5}, Ta^{+5}	$[MF_6]^-$, $[MF_7]^{=}$, $[MF_8]^{\equiv}$ oxyfluo complexes	$[MOF_5]^{=}$ obtained in H_2O, others under special conditions of acidity and F^- ion concentration
V^{+3}	$[VF_6]^{\equiv}$; $[V(H_2O)F_5]^{=}$, $[V(H_2O)_2F_4]^-$	stable in H_2O
Group VI		
S^{+6}	$[SO_3F]^-$	hydrolyzes readily
Se^{+6}, Te^{+6}	?	probably form complexes, composition not known
Cr^{+3}	$[CrF_6]^{\equiv}$ $[Cr(H_2O)F_5]$	stable, very similar to Al complexes
Cr^{+6}	$[CrO_3F]^-$	salts can be recrystallized from H_2O
Mo^{+6}, W^{+6}, V^{+6}	numerous oxyfluo compounds $[M^{+6}O_3F_2]^{=}$; $[M^{+6}O_3F_3]^{\equiv}$ $[M^{+6}O_2F_3]^-$ $[M^{+6}O_2F_4]^{=}$	stable, can be crystallized without change
Group VI		
I^{+5}	$[IO_2F_2]^-$	
Mn^{+3}	$[Mn^{+3}F_4]^-$ $[Mn^{+3}F_5]^{=}$	hydrolyzes in water
Mn^{+4}	$[MnF_6]^{=}$	stable in water ? decomposed by water → MnO_2
Group VII		
Fe^{+3}	$[FeF_4]^-$, $[Fe(H_2O)F_5]^{=}$ $[FeF_6]^{\equiv}$	very stable, CNS gives no immediate test for Fe^{+++}, Ba^{++} does not precip. BaF_2 "Solutions do not attack glass"
Co^{+2}, Ni^{+2}	$[M(H_2O)F_3]^{=}$	
Pt^{+4}, Ir^{+4}	$[MF_6]^{=}$	not hydrolyzed by water
Os^{+8}	$[OsO_4F_2]^{=}$	decompose in water

References

1. A table of complex fluo-salts with literature references to 1926 is to be found in Gmelin's "Handbuch der Anorganischen Chemie", Vol. 5, p. 59
2. Ray, Z. anorg. allgem. Chem., 241, 165 (1939)
3. Pugh, J. Chem. Soc., 1937, 1046
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THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS

Fred Basolo

May 11, 1943

I. The Stereoisomers of Dichlorodiethylenediamine Platinic Chloride

Diethylenediamine platinous chloride has been oxidized to dichlorodiethylenediamine platinic chloride, $[Pten_2Cl_2]Cl_2$, by means of ozone (1), potassium permanganate (2), and chlorine (3). For this investigation the complex was prepared in a manner similar to that discussed by Betty Rapp (4):

$$H_2PtCl_6 \cdot 3H_2O \xrightarrow{SO_2} PtCl_2 \xrightarrow{en} [Pten_2]Cl_2 \xrightarrow{Cl_2} \underset{\text{trans}}{[Pten_2Cl_2]Cl_2} \xrightarrow{Ag_2CO_3} [Pten_2CO_3]CO_3 \xrightarrow{\text{alc. HCl}} \underset{\text{cis}}{[Pten_2Cl_2]Cl_2}$$

A definite proof of the cis and trans structures assigned above could be had by resolving the cis complex since it should exist in dextro and levo forms. This was tried (4) but failed due to the extreme solubility of the cis $[Pten_2Cl_2]Cl_2$.

It was believed that the corresponding bromo compound would be less soluble and perhaps resolvable. The bromo complex was thus prepared and attempts made to resolve it using the following resolving agents failed; α-bromo-d-camphor-π-sulfonic acid, ammonium-α-bromo-d-camphor-π-sulfonate, silver-d-tartrate, and ammonium-d-camphor-π-sulfonate. Since the first three resolving agents mentioned gave crystalline fractions, the fact that the complex could not be resolved can not be blamed upon the solubility of the cis $[Pten_2Br_2]Br_2$. It must thus be assumed that either the cis form rearranges to the inactive trans or that the dextro and levo forms have similar solubilities. To prevent possible rearrangement the carbonato complex was used with the above resolving agents but again the optically active isomers could not be separated. This method for proving the structure of the cis complex was abandoned as it seemed that the difference in solubility of the dextro and levo forms was not large enough to permit their separation.

It has been observed (5) that in coordination compounds negative groups activate the trans position. Chernyaev has called this the "Trans Effect" and used it in the preparation of many desired complexes. With this in mind the cis and trans isomers were treated with liquid ammonia and pyridine in hopes that the following reactions might be obtained at the conditions specified:

$$\text{trans}\,[Pten_2Cl_2]Cl_2 + Py \xrightarrow[\text{30 min.}]{\Delta} [Pten_2pyCl]Cl_3$$

$$\text{"} \quad + Py \xrightarrow[\text{6 hr.}]{\Delta} [Pten_2py_2]Cl_3$$

$$\text{"} \quad + \text{liq. } NH_3 \xrightarrow{-33^\circ} [Pten_2NH_3Cl]Cl_3$$

$$\text{"} \quad + \text{liq. } NH_3 \xrightarrow[\text{room temp.}]{\text{sealed tube}} [Pten_2(NH_3)_2]Cl_4$$

$$\text{cis}\,[Pten_2Cl_2]Cl_2 + Py \xrightarrow[30\ \text{min.}]{\Delta} \text{No Reaction}$$

$$\text{"} \quad + Py \xrightarrow[\Delta]{6\ \text{hr.}} [Pten_2py_2]Cl_4$$

$$\text{"} \quad + \text{liq. } NH_3 \xrightarrow{-33^\circ} \text{No Reaction}$$

$$\text{"} \quad + \text{liq. } NH_3 \xrightarrow[\text{room temp.}]{\text{sealed tube}} [Pten_2(NH_3)_2]Cl_4$$

Analysis of the above compounds have not yet been taken but merely by observation it seemed that in the cases labeled "no reaction" nothing happened.

Chernyaev (6) has also done some work on the tetramines of quadrivalent platinum. He prepared the chloro compounds and proved their structures by their solubilities, reaction of the cis form with sodium hydroxide, and the ease with which the trans complex could be reduced. Similarly the supposed cis $[Pten_2Cl_2]Cl_2$ formed a black precipitate upon standing with a 10% solution of sodium hydroxide, while under the same conditions the trans showed no reaction. Polarographic studies were attempted to compare reduction potentials of the two isomers but in both cases the complex was such a strong oxidizing agent that this proved useless. Potentiometric titrations using standard $FeSO_4$ and KI solutions failed to give the expected break in the curve. Under exactly similar conditions at 67-68° it was noted that $K_2C_2O_4$ reduced the cis form in about seven minutes whereas the trans form required about twenty minutes. This is contrary to what was expected.

Measurements of dipole moments would definitely establish the structure of the two forms. This was tried by means of dielectric constants of aqueous solutions. No results were obtained perhaps due to the cell used -- the cell is being modified. X-ray diffraction patterns were taken on the powder and the two forms are definitely different as indicated by the different bands.

The absorption spectrum of a large number of coordination complexes is known. The metallic complexes have absorption bands which start in the visible and also occur in the ultraviolet. These bands have been designated first, second, and third as you go toward the shorter wave length. The third band is assumed (7) to be due to a pair or pairs of negative groups coordinated in trans positions. Ultraviolet absorption spectra of cis and trans $[Pten_2Cl_2]Cl_2$ showed a third band at a wave length of 2575 A. for the supposed trans form while the cis lacked such a band.

To test the validity of the above theory absorption spectra of the following complexes were taken:

Presence of third band	Absence of third band
trans $[Coen_2Cl_2]Cl$	cis $[Coen_2Cl_2]Cl_2$
trans $[Co(NH_3)_4(NO_2)_2]Cl$	cis $[Co(NH_3)_4(NO_2)_2]Cl$
	cis and trans $[Co(NH_3)_4Cl_2]Cl$
	cis and trans $[Coen_2(NH_3)_2]Cl_3$
	red and purple $[Co(NH_2CH_2COO)_3]$
	$[Coen_3]Cl_3$
	$[Cren_3]Cl_3$

The above compounds seem sufficient to prove that the third band is due to the trans negative groups and not to the coplanar rings of the coordinated ethylenediamine. Trans $[Co(NH_3)_4Cl_2]Cl$ failed to give a third band due to its ease of aquation.

References

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II. Studies on the Configuration of Cadmium, Zinc, and Platinum in Complex Ammines.

Although the absolute configurations of a pair of optical isomers are not known for any compound at the present time, the relative space positions of some compounds may be found if the configuration of a given compound is designated.. This has been successfully carried out with complexes of cobalt, chromium and rhodium (1, 2). These space relationships were found by three independent means: 1. Delpine's "Active racemate" method (3), 2. Werner's solubility rule (4), and 3. circular dichroism or "Cotton Effect" (5).

Partial success has been attained (6) in relating the generic configurations of tri-diammines of cadmium, zinc, and platinum. Using Werner's solubility rule Clapp was able to show that d- $[Cden_3]^{++}$, d- $[Znen_3]^{++}$, and l- $[Pten_3]^{++++}$ have the same generic configurations. He also established that $[Cd\ d\text{-}pn_3](NO_3)_2$ is isomorphous and apparently enantiomorphous with $[Cd\ l\text{-}pn_3](NO_3)_2$ and $[Zn\ l\text{-}pn_3](NO_3)_2$ but failure to prepare crystalline $[Pt\ l\text{-}pn_3](CO_3)_2$ was the shortcoming of this method of active racemates.

It is believed that if dextro and levo butylenediamine be used the corresponding platinum complex would be sufficiently insoluble to form crystals. At present butylenediamine has not been successfully resolved.

An attempt has also been made to use some amino alcohols furnished by The Commercial Solvents Co. These complexes are extremely unstable and difficult to prepare in crystalline form. A complex formed by heating cadmium chloride with 2-amino-1 butanol was analyzed for chloride and found to be $[Cd(Bno)_2Cl_2]$. It thus seems as if these will not be useful.

Another possibility may be the use of optically active trans 1,2 diaminocyclopentane or 1,2 diaminocyclohexane.

References

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DETERMINATION OF COMPLEX FORMATION

Philip S. Baker May 18, 1943

I. Introduction

Study of complex formation has been limited in the past by a dearth of good methods for determining whether coordination has actually occurred or not. We propose a method which depends upon the measurement of slight volume changes which occur when complexing occurs.

II. Historical

A. Hittorf apparently was the first to recognize that abnormal behaviour of certain electrolytes could be explained by assuming complex formation. He discovered that for the anion, the migration ratio frequently increased rapidly with increase in concentration of salts, and sometimes even became greater than unity.

B. Methods of measurement.

1. Chemical method - $AgNO_3$-KCN system.
2. Ionic migration method.
3. Distribution method.
4. Solubility method - rather theoretical.
5. Electrical potential method - depends upon the differences in the potential of an electrode dipping into a solution of the ions.
6. Mathematical method.
7. Cryoscopic method - LeBlanc and Noyes.
8. Viscosity maxima - doesn't always work.
9. Magnetic susceptibilities.
10. Molecular conductivity.
11. Heat of solution.
12. Refractive index.
13. Oxidation-reduction potentials.
14. Density method.

III. Theoretical.

Our proposed method is based on hydration theory, and on the probability that in most cases where complex formation occurs, there will be a change in volume due to the substitution of anions or molecules of different sizes for the water molecules.

Discussion of apparatus.

IV. Data.

V. Discussion

VI. Bibliography

1. Hittorff, Pogg. Ann. 89 177; 98 1; 103 1; 106 337, 513
2. Jacques, Complex Ions in Aqueous Solution, Longmans, Green and Company, London, 1914
3. Jakowski, Zeit. phys. Chem. 13 539; 18 585; 19 201. (1894-5-6)
4. Numerous Chem Abstracts.

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1943 - 1944

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ISOMERISM - ORGANIC AND INORGANIC

John C. Bailar, Jr. October 26, 1943

I. Definition of Isomerism
   A. Webster's dictionary: "Composed of the same elements united in the same proportion by weight, but differing in one or more properties owing to differences in structure."
   B. Polymers
   C. Polymorphs
   D. Allotropic Forms of Elements

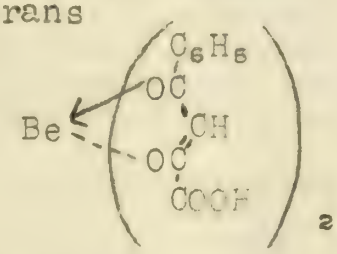
II. Factors which are essential to isomerism
   A. Covalent bonds
   B. Resistance to oxidation and reduction

III. Types of Isomerism
   A. Structural, with complete change of function. Resembles the isomerism of C_2H_5OH and CH_3OCH_3
      1. $NH_2O(SO_3H)$ and $NHOH$
      2. $Mn\begin{matrix}O\\O\end{matrix}$ and $Mn\begin{matrix}O\\O\end{matrix}$ SO_3H (This has no counterpart in organic chemistry)
      3. $[Co(NH_3)_5(NO_3)]^{++}$ and $[Co(NH_3)_4(NH_2OH)(NO_2)]^{++}$ (1)
   B. Nitro and Nitrito
      1. $[CO(NH_3)_5(NO_2)]^{++}$ and $[Co(NH_3)_5ONO]^{++}$
   C. Chain Isomerism (Resembles the isomerism of normal and iso-compounds, or ortho, meta, and para benzenoid compounds)
      1. $\left[\begin{matrix}(NH_3)_3 & & (NH_3)_3\\ & CO\begin{matrix}OH\\OH\end{matrix}CO & \\ Cl & & Cl\end{matrix}\right]^{++}$ and $\left[\begin{matrix}(NH_3)_2 & & \\ & CO\begin{matrix}OH\\OH\end{matrix}CO & (NH_3)_4\\ Cl_2 & & \end{matrix}\right]^{++}$
   D. Isomerism of Salts --totality of ions is constant (Compare the isomerism of $C_2H_5COO^-NH_4^+$ and $CH_3COO^-\ CH_3NH_2\cdot H^+$)
      1. Coordination Isomerism
         $[CO(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_6][CO(NO_2)_6]$
         $[CO(NH_3)_6][CO(NO_2)_6]$ and $[CO(NH_3)_4(NO_2)_2][CO(NH_3)_2(NO_2)_4]$
         $Ag_2(HgI_4)$ and $AgHg(AgI_4)$ (2)
      2. Ionization Isomerism
         $[CO(NH_3)_5Br]SO_4$ and $[CO(NH_3)_5SO_4]Br$
      3. "Simple" Salts. Usually, mutual oxidation and reductions take place, so one ion pair is too unstable to exist
         $UOSO_4$ and UO_2SO_3
         Thallous hypochlorite and thallic oxychloride
         Platinic sulfite and platinous dithionate
         Phosphonium nitrate and ammonium metaphosphate
      4. Cases in which the ions are identical except for charge
         cerous ferricyanide and ceric ferrocyanide
         thallous metaphosphate and thallic phosphite
   E. Tautomerism
      1. Phosphorus Acid (3)

F. Polymerism (compare isoprene and rubber or acetylene and benzene)
   1. $(PNCl_2)_x$ (4)
   2. $(HF)_x$ and $(H_2O)_x$
   3. "Hexameta phosphates"
   4. $[CO(NH_3)_3(NO_2)_3]$ and $[CO(NH_3)_6][CO(NO_2)_6]$

G. Geometric -- cis and trans (compare maleic and fumaric acids)
   1. 4-covalent planar -- $[Pt(NH_3)_2Cl_2]$, etc.
   $[Pt(NH_3)(NH_2OH)(NO_2)Py]$ Cl. There is no counterpart to this in organic chemistry. (5)
   2. 6-covalent --- $[CO(NH_3)_4Cl_2]$ Cl, etc.

H. Optical
   1. Due to crystalline form--quartz, cinnabar, sodium chlorate, etc
   2. Spirans



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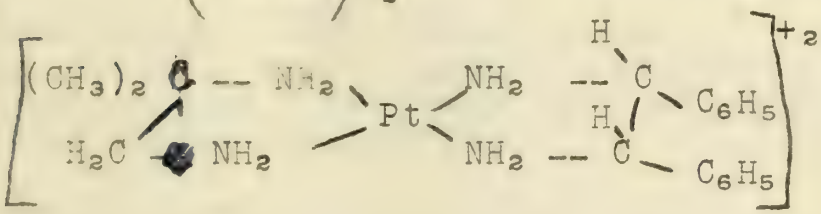
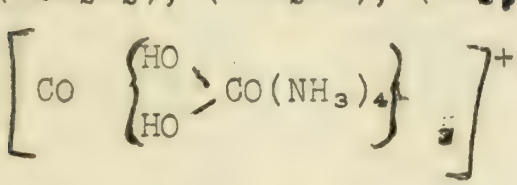
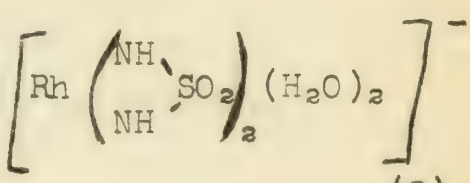


(7)

   3. Asymmetric hexacovalent metal atom
   (CO abcdef) -- fifteen pairs of mirror images
   (COA_2a_2), (COA_2ab), (COA_2a)



(8) and cis



(9)

   4. Asymmertic Octacovalent metal atoms

$K_4[U(C_2O_4)_4]$ (10)

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Separation of Erbium from Yttrium by Fractional Precipitation of the Ferrocyanides

H. E. Kremers

November 2, 1943

I. Introduction

A. Preliminary separation of rare earth mixture by double sulfates followed by bromate fractionation of double sulfate mother liquors.
B. Continued fractionation of bromates finally gives fractions containing essentially yttrium and erbium.
C. Separation of Yttrium from erbium can be accomplished by
   1. Basicity methods
      a. Nitrite method
      b. Basic nitrate separation
      c. Fractional precipitations with ammonia, urea, etc.
   2. Ferrocyanide precipitation

II. Characteristics of rare earth ferrocyanides

A. Composition: $KR[Fe(CN)_6] \cdot n\ H_2O$
B. Solubilities favor separation of yttrium from erbium.
C. Precipitation from strong acid solutions give filterable ferrocyanide precipitates.

III. Method of ferrocyanide precipitation.

A. Precipitation procedure. Addition of NH_4Cl increases solubility of the precipitates.
B. Recovery of rare earths.
C. Fractionation of erbium - yttrium mixtures.
   1. Control by spectrophotometric analysis.
   2. Combination of fractions according to analysis is necessary for most efficient operation.
D. Disadvantages of the method
   1. Some loss of rare earth material.
   2. Requires extensive mechanical manipulation.
E. Advantage. Extremely rapid separation.

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EXPERIMENTAL STUDY OF GASES

Donald Ray Martin

November 9, 1943

I. Historical

The technic had its beginning in Professor P.A. Guye's Laboratory in Geneva, Switzerland. Dr. A.F.O. Germann worked with gases in that laboratory and brought the technic to Western Reserve University. Due to Professor E.W. Morley's work and also to the nature of the research being undertaken by Dr. Germann, Professor H.S. Booth became interested in working with fluoride gases and with his students developed the modern technic.

II. Generation of Gases

A. (Slide 1) The Swarts Generator. (4)

III. Purification of Gases

A. Guye first used liquid air to fractionally distill gases.
B. Ampule to ampule fractionation; 30 required to obtain BF_3 with a constant value for its density. (8)
C. Automatic Fractionating Column (2)
   1. Construction of reflux cooling head
   2. (Slide 2) Still head cooling with acetone - solid carbon dioxide.
   3. (Slide 3) Still head cooling with liquid air.
   4. Fractionating column proper with Dufton wire spiral.(6) Concetric tube packing also used. (9)
   5. Reflux return through glass dripper
   6. Insulating jacket -- 90 cm. length, evacuated, silvered with longitudinal windows.
   7. Still pot heat input.
   8. (slide 4) Automatic stopcock
   9. (slide 5) Reflux ratio check.

IV. Physical Properties

A. Molecular weight
   1. (slide 1) Edwards Density Balance
   2. Dumas bulb.
B. (slide 6) Freezing point(2, 3)
   1. Thermocouple calibration
   2. (Slide 7) Micromax Recording Potentiometer produces cooling curves.
C. (Slide 3) Vapor pressure and boiling point.
   1. Germann manometer. (7)
D. Critical temperature and pressure. (5)

V. Thermal Analyses of Liquified Gases (,1,3)

A. (Slide 8) Establishing the mole fractions.

B. (Slide 9) Determining the freezing point.

VI. Storage of gases

A. Ampules with refrigerant
B. (Slide 10) Glass balloons (20 liters) using a mercury cut-off (3)
C. Cylinders.

VII. Bibliography

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Roll Call

November 16, 1943

V. C. Boekelheide talked on Grosse's article on Catalysis (2nd Eng. Chem.)

Therald Moeller talked on Wiberg and Johanssen, Naturwissenschaften 29, 320 (1941).

$$Me_3Ga \xrightarrow[\text{Glow Discharge}]{H_2} GaH_2MeGaMe_3$$

$$GaH_2MeGaMe_3 \xrightarrow{Et_3N} GaMe_3.Et_3N + Ga_2H_6$$

Not enough electrons for two electron bonds.

Longuet-Higgens and Bell, J.C.S. 1943, 250-5 have a new theory of boron hydrides.

They write B_2H_6:

This is not the usual type of H bond.

This explains some reactions of B_2H_6.

$$B_2H_6 + CO \longrightarrow 2BH_3.CO$$

$$B_2H_6 + NMe_3 \longrightarrow 2BH_3.NMe_3$$

We can get a tetraalkyl derivative of B_2H_6, in which two R groups are on each B. This shows that 2H are different from the other four.

J. A. Mattern talked on atomic structure.

Schiff - Gen. Elec. Review 40, 504 (1937).

CLASSIFICATION OF CARBIDES

Elizabeth W.Peel

November 23, 1943

I. According to the reaction with water; based on chemical properties, (1, 3).

A. Inert carbides -- Those not attacked by water or dilute acids. This class includes carbides of the elements whose oxides are acidic. The class is really heterogeneous, but is not further subdivided by this classification.

B. Reactive carbides. Those decomposed by water or dilute acids. Further subdivided, according to the products of decomposition.

1. Methane derivatives. Carbides hydrolyzing to methane, sometimes accompanied by other hydrocarbons, but never acetylenes. Carbon atoms in lattice separated by metal atoms, as in Fe_3C and Be_2C. Ni, Co, Mn etc. Hydrolysis probably gives $-CH_2-$, which then is hydrogenated or dimerizes.

2. Acetylene derivatives. Carbides hydrolyzing to acetylene, sometimes with other hydrocarbons. Acetylide linkage ($-C\equiv C-$) present already in the lattice before hydrolysis, but maybe reduced if the metal is oxidized in the hydrolysis. Examples, CaC_2, $Ce_2(C\equiv C)_3$ given acetylene; CeC_2 gives acetylene with more saturated hydrocarbons. Acetylides only formed by metals with larger ionic radii, necessitated by the tetragonal structure.

3. Allylene derivatives. Carbides hydrolyzing to give allylene, $CH_3C\equiv CH$. Mg_2C_3 the only one known. A pre-formed three-carbon chain in the carbide is indicated.(4)

I. Structure classification. Based on the structure of the molecules; developed by Antropoff (2).

A. Valence compounds. Those in which the elements exhibit a normal valence.

1. Polar, or salt-like, carbides. Electrovalent, with ionic lattices.

2. Non-polar carbides. Covalent, with molecular lattices; volatile.

3. Diamond-like, or tetrahedral, carbides. Covalent, like the non-polar carbides, but with infinitely larger molecules, hence not volatile .

4. "Intermolecular" compounds, such as the condensed hydrocarbons; will not be discussed here.

B. Atomic compounds or "packing" compounds. Those in which the element does not show its normal valence.

1. Alloy-like carbides. Like alloys of definite composition Composition independent of valence, dependent on geometric and energetic factors.

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	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	----VIII----			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0
1	H_4C																	He
2	Li_2C_2	Be_2C											B_4C	C	$(NC)_2$	O_2C O_2C	F_4C	Ne
3	Na_2C_2	Mg_2C_3 MgC_2	(Al_4C_3)										Al_4C_3	SiC	P_2C_6	S_2C SC	Cl_4C	A
4	K_2C_2	CaC_2	Sc_4C_3	TiC	VC	Cr_3C_2 Cr_4C MoC	Mn_3C	Fe_2C	Co_3C	Ni_3C	Cu_2C_2 CuC_2	Zn	Ga	Ge	As_2C_6	Se_2C	Br_4C	Kr
5	Rb_2C_2	SrC_2	YC_2	ZrC	CbC	Mo_2C WC	Ma	Ru	Rh	Pd	Ag_2C_2	Cd	In	Sn	Sb	Te_2C	I_4C	Xe
6	Cs_2C_2	BaC_2	R.E., e.g.: LaC_2	Hf	TaC	W_2C	Re	Os	Ir	Pt	Au_2C	Hg_2C_2 HgC_2	Tl	Pb	Bi	Po	(85)	Rn
7	(87)	Ra	Ac	ThC_2	Pa	UC_2												

Figure I

Polar, salt-like carbides

Diamond-like carbides

Alloy-like carbides

Nonpolar, volatile carbides

Virginia Bartow December 7, 1943

I. Life
- Born March 31, 1811 -- Göttingen
- Education -- Göttingen, Paris, Berlin, Vienna
- Member of the faculty of the universities in Göttingen, Cassel, Marburg, Breslau and Heidelberg
- Retired 1889
- Died August 16, 1899 -- Heidelberg

II. Scientific Achievements
- Thesis: Hygrometers
- Early papers -- Antidote for arsenic (sole medical paper)
  - -- Analysis of allophane
  - -- Double cyanides (all a "Kleiner Vorversuch)
- Cacodyl -- (practically the only organic research)
- Composition of gases in furnaces - practical applications
  - Book on "Gasometric Methods"
- Carbon-Zinc battery Zinc-Carbon-chromic acid battery
  - Thermopile of Cu pyrites and Cu
- Photometer
- Ice and vapour calorimeters
- Measurement of the chemical action of light
- Spectrum analysis with Kirchhoff
  - Discovery of caesium and rubudium
- Spark spectra of rare earths
- Chemical geology
- Separation of the metals of the platinum group
- Firing of gunpowder

III. Additional equipment
- Filter pump
- Bunsen burner

IV. Honors

V. Character and anecdotes

VI. Students

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Compounds of the "Inert Gases"

J.V. Quagliano

December 14, 1943

I. Introduction

Early unsuccessful attempts to prepare compounds of the inert gases. Theory of "nullivalence." "The chemical elements without chemistry."

II. Theoretical considerations for the reactivity of inert gases

1. Maximum number of electrons in quantum group, n, is $2n^2$ -- only satisfied by He and Ne, hence inert gases can accept electrons.
2. Inert gases can coordinate by giving electrons to an acceptor.
3. Polarization of an inert gas atom by a central ion.
4. Field Valency
5. Excitation of inert gas atoms to higher levels.

III. Hydrates of the inert gases. $R(H_2O)_6$ (1,2)

Formation of hydrates receives additional support from work of Tannung (3) who shows that in all cases the solubility of the inert gases decreases with temperature.

IV. Coordination of inert gas Argon with BF_3 (4)

In these compounds boron acts as acceptor of electrons.

$Me_2O \longrightarrow BF_3$, $H_2S \longrightarrow BF_3$, $A \longrightarrow BF_3$

Thermal analysis of system Argon -- Boron trifluoride

1. Freezing point of mixture of BF_3 and A increases with pressure at first and then become independent of further increase in pressure ($A + XBF_3 \rightleftharpoons A\,XBF_3$)
2. Maxima correspond to ratios, $A\,X\,BF_3$, x = 1,2,3,6,8,16
   a. Compounds which X =1, 2,3, are formed by coordinate links in which Argon donates electrons to complete boron octet.
   b. Compounds which x=6, 8, 16; the BF_3 molecules are linked directly to Argon atom and rest of molecules linked to boron trifluoride molecules via their fluorine atoms.

V. Helides prepared in discharge tube.

1. Helides of mercury $Hg\ He_2$, HgH_3 ($HgHE_{10}$) (6)
2. Helide of tungsten WHe_2 (7)

VI. Coprecipitation of inert gases with isomorphoric compounds (8,9)

1. The precipitation and quantitative separation of the inert gases by isomorphic coprecipitation with hydrate of SO_2
2. The precipitation of $X6 \cdot 2C_6H_5OH$ in presence of crystal nuclei of $H_2S \cdot 2C_6H_5OH$

VII. Method of Electrical Discharge between Metal Electrodes in presence of inert gases.

1. "Chemical inertia" of the inert gases can be eliminated by a suitable process.
   a' Electric discharge at low and high pressures and low temperature
   b. Use of surface systems like metals activated by cathodic pulverization.
2. Evidence for chemical charges
   a. existence of fixed decomposition temperatures
   b. Appearance in X-Ray spectra of rings analogous to those given by amorphous compounds of Pt. with O or S.
   c. Fundamental stable charges of structural properties of Pt. (appearance, optical properties, density, passage from crystalline to amorphous state, solubility in HCl, HNO_3)
   d. Existance of a saturation of Pt. by He, reaching a maximum corresponding to Pt_3H5.

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COMPOUNDS OF CHLORINE AND THE MORE ELECTRONEGATIVE ELEMENTS.

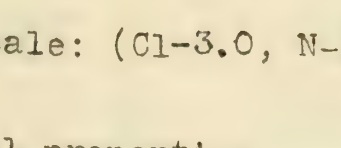
Robert W. Parry

December 21, 1943

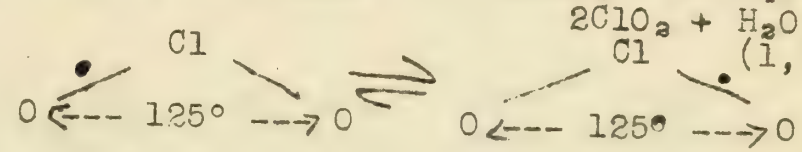
I. Introduction
   A. Electronegativity scale: (Cl-3.0, N-3.0, O-3.5, F-4.0)

II. General Characteristics
   A. Physical and chemical properties
      1. gas or comparatively low boiling liquid
      2. Highly reactive
   B. Bond types as related to electronegativity scale. Covalent to partially ionic

III. Compounds of the group
   A. Oxides
      1. Cl_2O
         a. Preparation -- $2HgO + 2Cl_2 \longrightarrow Hg_2OCl_2 + Cl_2O$ (etc)
            (3,) (4,) (1,)(2,)(5,)(6,)
         b. Structure



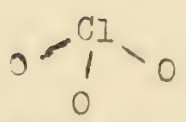
      2. ClO -- Never isolated; postulated as intermediate in reactions of oxides of Cl (2)
      3. ClO_2
         a. preparation - $3H_2SO_4 + 3KClO_3 \longrightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$ (1,2)
         b. structure



Resonating 3 electron bond (Pauling)

      4. Cl_2O_3 existence doubtful (8)
         a. preparation - $4KClO_3 + 2H_2SO_4 \xrightarrow{*} 2H_2O + 2K_2SO_4 + Cl_2O_7 + Cl_2O_3$
            * in presence of undecylinic acid
         b. structure not established
      5. $ClO_3 + Cl_2O_6$
         a. preparation - $ClO_2 + O_3 \xrightarrow{15°C} ClO_3 + O_2$ (9) (2) ← preparation
            ↑ Bp. 82°
         b. structure

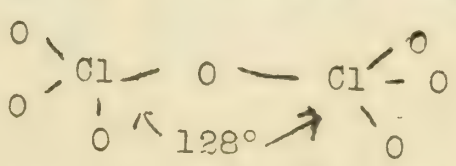
Cl_2O_6 (liquid) $\rightleftharpoons$ $2ClO_3$ (gas)



probably non planar

$Cl_2O_5 \rightarrow Cl_2O_3 + Cl_2O_7$ and
$Cl_2O_5 \rightarrow ClO_2 + Cl_2O_7$

      6. Cl_2O_7
         a. preparation -- $2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + P_2O_5 \cdot H_2O$
         b. structure



non planar (11)

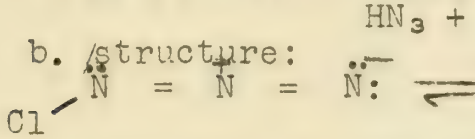
6a. ClO_4 was prepared as a free radical by Gomberg

7. Summary of bond relations of 4 established oxides: (2)

	Cl_2O	ClO_2	ClO_3	Cl_2O_7
ΔH	-21.7 Kcal/g	-26.6	-37.0	-63.4
ΔU	-22.0 mole	-26.9	-37.6	-65.4
Total bond energy	+93.7 "	+119.0	+167.0	+402.0
Ave. bond energy	47.0 "	59.5	55.6	50.3
Kc(O-Cl)A°	1.71 A	1.57	---	----
total weakening	10 KCal/g mole	---	---	14
total strengthening	----	15	11	----

B. Nitrogen Compounds

1. NCl_3
   a. preparation $NH_3 + 3HOCl \rightleftharpoons NCl_3 + 3H_2O$
      or electrolysis of NH_4Cl soln. (12)
   b. Structure
      Direct evidence not available
      bond purely covalent. Bond energy - 38.4 Kcal
   c. cause of instability (1)
2. $Cl-N_3$
   a. preparation $AgN_3 + Cl_2 \longrightarrow AgCl + ClN_3$ (13)
      $HN_3 + HOCl \rightleftharpoons ClN_3 + H_2O$ (13)
   b. structure:



      relation of structure to stability

C. Fluorides

1. ClF
   a. preparation $Cl_2 + F_2 \longrightarrow 2ClF$ (15)
   b. properties (14,15) Chemically similar to F_2, but slightly more active
   c. structure
      Cl-F bond energy 86.5 k cal/mole
      Bond approximately 30% ionic

      Cl-Cl is 57.8 kcal/mole
      F-F is 63.5 kcal/mole
2. ClF_3
   a. preparation (16) $ClF + F_2 \longrightarrow ClF_3$
      $Cl_2 + 3F_2 \longrightarrow 2ClF_3$
   b. properties -- extremely reactive (16)
   c. structure (17)
      Flourines grouped around Cl at corners of equilateral triangle.

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PHYSICAL PROPERTIES OF COMPOUNDS OF CHLORINE AND THE MORE ELECTRONEGATIVE ELEMENTS

Compound	Mol. wt.	Description	Melt pt.	Boiling pt.	ave. bond energy	Dev. From Normal	Remarks
A. oxides							
1. Cl_2O	86.9	red brown liquid or yellow red gas	-20	3.8	47.0 *	-5.0	explosive
2. ClO	—	never isolated	---	---	----	---	-----
3. ClO_2	67.5	orange red crystals red-yellow gas	-59	9.9	59.5	+7.5	Explosive
4. Cl_2O_3		not isolated	---	---	----	----	-----
5. $ClO_3 + Cl_2O_6$		red liquid orange crystals	3.5	82	55.6	+3.6	Explosive
6. Cl_2O_7	182.9	colorless vol. oil	-91.5	82	45.0 52.0	-7.0 0	Decomooses slowly at room temperature
B. nitrogen							
1. NCl_3	120.4	yellow oil	<-40	<71	38.4	----	Highly unstable
2. $Cl-N_3$	77.5	yellow orange liquid	-100	-15	----	----	Highly unstable
C. flourides							
1. ClF	54.5	colorless gas gold liquid	-154	x * -101	86.4	0	Reactivity similar to F₂
2. ClF_3	92.5	nearly colorless gas light green liquid	-83	✓ 11	----	----	More reactive than Cl-F

*-B.E. = K cal/mole.
Normal Cl-O bond = 52 Kcal/mole (2)
x- calc. critical temp. = 140°C
✓- Calc. critical temp. = 154"c

The Structure of the Nitrogen Molecule

H.A. Laitinen

January 4, 1944

I. Theory of Lewis, modified by Pauling

A. Triple bonded covalent structure
B. Stabilization by resonance between :N:::N: and $:\overset{+}{N}:\overset{-}{N}:$
C. Criticism of resonance picture

II. Heitler-London theory, modified by Pauling and by Slater

A. Attractive force between atoms due to splitting of original energy state of separated atoms into two states of different energy.
   1. Exchange or resonance energy
   2. Stable and activated (or sometimes unstable) states of resulting molecule.--example: interaction of hydrogen atoms.
B. Relation of electron spin to energy of interaction -- the greater the number of pairs of electrons of opposed spins, the greater the stability of the molecule. Example: The ground state and activated and unstable states of N_2.
C. The valence theory of Heitler and London: The number of unpaired electrons in the atom (normal or excited) is the valence of the atom.

III. Theory of Langmuir (1919), the fore-runner of modern "molecular orbital" pictures.

A. Similarity of physical properties of CO, N_2 , and A.
B. Chemical inertness of CO and especially N_2.
C. Stable octet, with two "imprisoned" electrons.

IV. Theory of Hund and Mulliken, extended by Herzberg and Lennard-Jones

A. A molecule (example N_2) is intermediate between the "United atom" (Si) and the separated atom (N + N).
B. Splitting of energy levels of electrons in Si atom as nucleus in split into 2N nuclei and pulled a small distance apart.
C. Splitting of energy levels of N atoms as they approact from infinity to a relatively large nuclear separation.
D. The nitrogen molecule as an intermediate between B and C.
   1. Molecular orbitals or energy levels in N_2 molecule.
   2. Eight bonding and two anti-bonding electrons.
   3. First excited state -- very large excitation energy accounts for inert character. Binding strength much less (larger internuclear distance, smaller force constant.)

V. Theory of Fajans

A. Symmetry of molecules (and ions)
   1. On basis of crystal structure, molar volume, molar refraction the groups $C_2^=$, CN^-, N_2, CO, NO^+ have outer shells which deviate only slightly from the spherical symmetry of the inert gases.

2 Molar refraction shows N_2 has the same symmetry relative to Ne that H_2 has to He.

B. Force constant, nuclear distance

Consider the series C_2, N_2, O_2, F_2
BeO, CO, NO, O_2

In each case the force constant is a maximum, the internuclear distance is a minimum, with 10 valence electrons.

C. Molecular Quantization

1. Nitrogen structure $(N^{+5})\ I^2\ \ II^8\ (N^{+5})$
2. Molecule P_2 $(P^{+5})\ II^8\ III^2\ (P^{+5})$
   or more probably $3^{2,2}\ (P^{+5})\ II^8\ (P^{+5})\ 3^{2,2}$

D. Criticisms by and of Fajans

1. Hund-Mulliken theory does not explain instability of P_2 and stability of N_2. But Fajans theory does not <u>predict</u> although it may account for instability of P_2.
   (NOTE) The molecule P_2 is stable with respect to the atoms, but not with respect to P_4.
2. The addition of the last electron to positive ions of the molecules H_2, N_2, HCl and HO increases force constant. Hence, the last electron is bonding. From the fact that the relative increase is larger the smaller the number of electrons, Fajans concludes that all ten of the N_2 valence electrons are bonding. However, according to Hund-Mulliken the least firmly bound electron in N_2 is bonding.

VI. Conclusion

A. The method of molecular orbitals appears to be the best approach to the structure of small, multiple bonded molecules.

B. The Fajans theory needs a great deal of development, but may lead to a closer understanding of the chemical, rather than physical, stability of molecules, particularly the simpler ones.

C. The Lewis-Pauling method is, and will continue to be, the most general and readily applicable theory, particularly for larger molecules.

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THE MAGNETO-OPTIC METHOD OF ANALYSIS

William E. Morrell January 11, 1944

I. History and development of the method. (1,2,3,4-I, 29) (See (4-I), particularly, for many additional references on this and most of the following topics.)

II. Description

A. Apparatus. (1,2,3,4-II)

B. Effect attributed to time-lags in Faraday Effect. (1,2,3,4-I)

III. Applications of the method.

A. Qualitative analysis. (5,8,12)

B. Quantitative analysis. (4-III, 9) - Found Sn^{++} ion.

C. Following course of reactions. (10,11,34,36)

D. Discovery of new elements. (3) - algae generate AcHO

$CO_2 + H_2O \rightarrow HCHO$

E. Discovery of isotopes. (1,2,3,7)

IV. Criticisms.

A. "Minima aren't due to time-lags in the Faraday Effect." (15, 16) (Very possible, but this doesn't affect their existence.)

B. "Results on isotopes don't agree with results obtained by mass spectrograph."

1. "Disagree in number of isotopes." (17,18,19,39c)

2. "Announced orders of abundance are impossible." (17,19) (Someone apparently did slip in interpretation on Bi and Tl.)

C. "We couldn't get reproducible minima." (16,21,22,23,24,25,26, 27)
(Reproducible minima apparently do exist, Hughes' photographic evidence has not been refuted. (13,14). Allison used photoelectric cell successfully. (2,3). There are many references which indicate the actuality of reproducible minima. See especially (5) to (15) here.)

D. "Reproducibility is due to physiological or psychological factors." (21,22,26,28)
(Undoubtedly some observers have been influenced by such factors, but these factors cannot explain the photographic evidence (13,14), for example.)

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Determination of the Compositions of Complex Ions by the Method of Continuous Variations

Therald Moeller January 18, 1944

I. Introduction
   1. Compositions of complex ions existent in solutions
   2. Development of the method in terms of the equilibrium
      $$A + nB \rightleftharpoons AB_n \quad (8,17)$$
   3. The general experimental procedure
   4. Properties of solutions amenable to this treatment
      a. Refractive index
      b. Absorption of light

II. Use of Refractive Index Determinations (14-16) $KCl + CdCl_2 \rightarrow CdCl_3^-, CdCl_4^=, CdCl_5^{---}$

III. Use of the Absorption of light (1-13,17)
   1. Historical approach
      a. The method of Shibata, et al (12,13,3,4)
      b. Job's method of continuous variations (5-10, expecially 8)
      c. Modified procedure of Vosburgh (17,1,2)
   2. Theoretical justification for applicability of the method (17)
      a. To systems in which a single complex ion is formed
         1. Extension of treatment in I-2 to show maximum or minimum in light absorption at solution compositions corresponding to maximum concentration of AB_n
      b. To systems in which more than one complex ion are formed
         1. Extension of treatment in terms of a second equilibrium $AB_n + qB \rightleftharpoons AB_{n+q}$
         2. Results based upon use of selected wave lengths
   3. Typical cases to illustrate application of the modified procedure where one or several complexes result
   4. Investigation of the system $Cu^{++} - Cl^-$ (11)
      a. Absorption spectra for solutions containing cupric nitrate and added chloride
      b. Establishment of the existence of the $CuCl_4^=$ ion
      c. Interpretation of results

IV. Results Typical of Many Investigations -- Table I

V. Conclusion
   1. Limitations of the method

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$A + nB = AB_n$

Same molar conc of A and B

at equilibrium:

$$c_1 = M(1-x) - c_3 \quad (1)$$
$$c_2 = Mx - nc_3 \quad (2)$$
$$c_1 c_2^n = Kc_3 \quad (3)$$

$\frac{dc_3}{dx} = 0$ when c_3 is at a maximum

Differentiating (1), (2), (3)

$$dc_1 = -Mdx - dc_3 \qquad dc_1 = -Mdx$$
$$dc_2 = Mdx - ndc_3 \qquad dc_2 = Mdx$$
$$c_2^n dc_1 + nc_2^{n-1} c_1 dc_2 = Kdc_3$$

$n =$ ~~a function of~~ $\frac{x}{1-x}$

We pick some property which can be measured as x varies

Substituting from above

$$-c_2^n Mdx + nc_2^{n-1} c_1 Mdx = Kdc_3$$
$$-c_2^n + nc_2^{n-1} c_1 = 0$$

Substitute equations (1) + (2) to get

$$n = \frac{x}{1-x}$$

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TABLE I

Typical Complex Ions Established by the Method of Continuous Variations

System Investigated	Complexes Indicated	Method Employed	Reference
$Mg^{++}-Cl^-$	MgX_3^-	Ref. index	14
$Cd^{++}-X^-(Cl^-,Br^-,I^-)$	$CdX_3^-, CdX_4^=, CdX_5^{\equiv}$	"	15
$Cd^{++}-X^-(Br^-,I^-)$	$CdX_4^=$	Light abs.	8
$Hg^{++}-Cl^-$	$HgCl_3^-, HgCl_4^=, HgCl_5^{\equiv}$		
	$HgCl_6^{\equiv\equiv}$	"	12,3
	$HgCl_3^-$	"	8
	$HgCl_3^-, HgCl_5^{\equiv}$	Ref. index	15
$Hg^{++}-Br^-$	$HgBr_4^=, HgBr_5^{\equiv}$	Light Abs.	3
	$HgBr_4^=$	"	8
$Hg^{++}-I^-$	$HgI_4^=$	"	3,8
$Co^{++}-X^-(Cl^-,Br^-)$	CoX^+, CoX_3^-	"	9
$Cu^{++}-Br^-$	$CuBr^+, CuBr_3^-$	"	9
$Cu^{++}-Cl^-$	$CuCl_4^=$	"	11
$Cu^{++}-NH_3$	$Cu(NH_3)_2^{++} Cu(NH_3)_4^{++}$	"	17
$Cu^{++}-en$	$CuEn_2^{++}$	"	6,8
$Ni^{++}-en$	$Nien^{++}, Nien_2^{++}, Nien_3^{++}$	"	17
$Cu^{++}-dn$	$Cudn^{++}, Cudn_2^{++}$	"	2
$Ni^{++}-dn$	$Nidn^{++}, Nidn_2^{++}$	"	2
$Fe^{++}-phen$	$Fephen_3^{++}$	"	1
$Fe^{+++}-SCN^-$	$FeSCN^{++}$	"	1

Ionization Potentials of the Elements

Atom	Electron Config.	1st	2nd	3rd	4th	5th	6th	7th	8th
H	1	13.530							
He	2	24.4764	54.142						
Li	2,1	5.368	75.282	121.86					
Be	2,2	9.2810	18.14	153.10	216.86				
B	2,3	8.33	23.98	37.75	258.1	338			
C	2,4	11.217	24.28	47.7	64.190	389.9	487		
N	2,5	14.48	29.47	47.17	(73.5)	97.428	(546.7)	663	
O	2,6	13.550	34.93	54.88	77.0	109.19	137.482	(733)	866
F	2,7	18.6	34.6	(58.02)	(84.88)	(113.0)	(152.9)	184.0	(945.8)
Ne	2,8	21.47	40.77	63.2	.....	.....	.....	.....	.....
Na	2,8,1	5.116	47.0	70.72	.....	.....	.....	.....	.....
Mg	2,8,2	7.61	14.97	80	108.9	.....	.....	.....	.....
Al	2,8,3	5.96	18.75	28.32	(122)	153.4	.....	.....	.....
Si	2,8,4	8.12	16.27	33.30	44.95	(169)	.....	.....	.....
P	2,8,5	11.1	19.81	30.04	51.1	64.74	.....	.....	.....
S	2,8,6	10.31	23.30	34.9	47.08	(67)	87.67	.....	.....
Cl	2,8,7	12.96	23.70	39.7	47.4	67.7	(88.7)	113.7	.....
A	2,8,8	15.69	27.80	40.7	~~17.61~~	(78)	.....	.....	.....
K	2,8,8,1	4.321	31.7	46.5	.....	.....	.....	.....	.....
Ca	2,8,8,2	6.09	11.82	50.8	69.7	.....	.....	.....	.....
Sc	2,8,9,2	6.57	12.80	24.34	(72.2)	(97.0)	.....	.....	.....
Ti	2,8,10,2	6.80	13.60	27.6	44.66	(95.7)	.....	.....	.....
V	2,8,11,2	6.76	14.7	29.6	48.3	68.64	(122)	.....	.....

The above table gives the ionization potentials in volts for the elements in the atomic state. Doubtful values are indicated by parentheses. Dots indicate values not listed in the reference. The table is copied from Sherman, Chemical Reviews 11, 138 (1932). Sherman lists figures for the other elements also, and lists the original references. numbers in pen are from Rubber Handbook

THE OXIDATION STATES OF SILVER

John C. Bailar, Jr. February 29, 1944

I. Introduction

A. Position of silver between copper and gold in the Periodic table.

B. Most text books either ignore higher oxidation states of silver or deny them.

C. Higher oxidation states of silver were discovered by Ritter in 1804. The literature contains dozens of articles on them. The oxide and salts of divalent silver are easily prepared, and stable at ordinary temperatures almost indefinitely. The oxide of trivalent silver decomposes in a few hours.

II. Tripositive Silver

A. Electrolysis of solutions of silver nitrate (other salts behave similarly) deposits a black, crystalline, oxygen rich material on the anode.(1,2,3,18) This approximates the formula $Ag_7O_8NO_3 = AgNO_3 \cdot 2Ag_2O_3 \cdot 2AgO$, but if it is filtered and analyzed at once, the silver closely approaches oxidation number of 3. (18)

1. This loses oxygen rapidly at room temperature
2. Treatment with boiling water gives pure AgO
3. It dissolves in HNO_3, H_2SO_4, $HClO_4$, but not in H_3PO_4 or HF. These solutions give no test for peroxide.(3)
4. Suspended in water, it oxidizes Cr^{+++} to $CrO_4^{=}$, NH_3 to N_2, Mn^{++} to MnO_2 and MnO_4^-, H_2O_2 to O_2.(3)

B. Action of fluorine gas on solutions of silver salts gives a similar product.(13)

C. Action of hot dilute HNO_3 on AgO

D. The reaction of $AgNO_3$ and $Na_2S_2O_8$ gives a black precipitate, which if filtered and analyzed at once shows a ratio of available equivalents of oxygen to silver of 2:1 (Ag_2O_3). On standing this falls in three hours to 1.5:1 (3,4,5,6)

E. Malatesta prepared salts of the ions $[Ag(IO_6)_2]^{-7}$, $[Cu(IO_6)_2]^{-7}$, $[Ag(TeO_6)_2]^{-9}$ and $[Cu(TeO_6)_2]^{-9}$ (7)

F. Oxidation of VO^{++}, Mn^{++}, CH_3COCH_3, etc. by $S_2O_8^{=}$ is catalyzed by Ag^+. The rate of reaction is proportional to $[Ag^+]$ and $[S_2O_8^{=}]$, but not to VO^{++}, Mn^{++}, etc. (8, 9, 10). This indicates:

$$Ag^+ + S_2O_8^{=} \longrightarrow Ag^{+++} + 2SO_4^{=} \quad \text{(slow)}.$$
$$Ag^{+++} + 2VO^{++} + 4H_2O \longrightarrow Ag^+ + 2VO_3^- + 8H^+ \quad \text{(fast)}$$

G. Rate of oxidation of Ag^+ by ozone in nitric acid is proportional to $[Ag^+]$ and to $[O_3]$ (14)

$$Ag^+ + O_3 \longrightarrow AgO^+ + O_2 \text{ (gas)}$$

III. Dipositive Silver

A. Silver Difluoride. The action of flourine on silver[11,12], or silver halides.[12]

1. Silver foil or powder at 100-300° is vigorously attacked by fluorine to give a brown-black powder, AgF_2.
2. Silver halides react readily with fluorine to give the same product.
3. Properties
   a. Strongly paramagnetic
   b. Decomposes at about 450° to $AgF + F_2$
   c. Density 4.57-4.78
   d. Fluorinating agent (CCl_4 to CF_4)
   e. Liberates O_2 and O_3 from water
   f. Reacts violently with metals, C, S, P, H_2
   g. Changes SO_2 to SO_2F_2 and CO to COF_2
   h. In aqueous solution, $Cr^{+++} \longrightarrow CrO_4^{=}$, $I^- \longrightarrow I_2$

B. Argentic Salts in Acid Solution

1. Preparation
   a. $Ag^+ + O_3$ (in HNO_3) $\longrightarrow$ argentic compounds + O_2
      The compounds initially formed contain trivalent silver, but these quickly decompose to Ag^{++}.(14) Since the Ag^{++} decomposes slowly, a "steady state" of $[Ag^{++}]$ is reached.
      $Ag^+ + O_3 \longrightarrow AgO^+ + O_2$ (Gas) (slow)
      $AgO^+ + Ag^+ + 2H^+ \longrightarrow 2Ag^{++} + H_2O$ (fast)
   b. $PbO_2 + 2AgNO_3 + 4HNO_3 \longrightarrow 2Ag(NO_3)_2 + Pb(NO_3)_2 + 2H_2O$
      This gives as much as 90% yield. (20)
2. Proof that the silver is dipositive. (15)
   a. Analysis of the solution for total silver and for oxidizing power.
   b. Displacement of the steady state. Varying conditions of preparation raises available oxygen toward 2 equivalents per Ag atom, but never past 2.
   c. Magnetic susceptibility
3. Properties of the acid solution. (16)
   a. Powerful oxidizing agent ($Cr^{+++} \longrightarrow CrO_4^{=}$, $Ce^{+3} \longrightarrow Ce^{+4}$, $IO_3^- \longrightarrow IO_4^-$, $Tl^+ \longrightarrow Tl^{+++}$)
      Oxidation-Reduction Potentials of Some Couples.

	Volts
$F_2(g) + 2e \rightleftharpoons 2F^-$	2.88
$O_3(g) + 2H^+ + 2e \rightleftharpoons O_2(g) + H_2O$	2.07
$Ag^{++} + e \rightleftharpoons Ag^+$	1.914
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	1.77
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$	1.447
$PbO_2(s) + 4H^+ + 2e \rightleftharpoons Pb^{++} + 2H_2O$	1.444
$Ce^{+4} + e \rightleftharpoons Ce^{+3}$	1.44

   b. Silver is in a nitrate complex, as shown by increase in solubility by increasing concentration of NO_3^-, color, oxidizing potential of solution, and transference experiments. (18,19)

C. Argentic Oxide

a. Treat $Ag_7O_8NO_3$ with boiling water. (Boiling for 30 hours lowered the apparent formula to $AgO_{0.97}$) (18)

b. $Na_2CO_3 + K_2S_2O_8 + AgNO_3 \longrightarrow AgO$ (21)

c. AgO is paramagnetic (25)

D. Complex argentic ions.

a. $[Ag\ pyridine_4]^{++}$. Made by oxidizing a solution containing Ag^+ and pyridyine with $S_2O_8^=$ or electrolytically (23). Orange red, crystalline, paramagnetic (24,25) Isomorphous with the cupric (22) and cadmium salts (6).

b. $[Ag(dipyridyl)_2]^{++}$ and $[Ag(dipyridyl)_3]^{++}$ (24,25,26,27,28) Reddish brown, paramagnetic

c. $[Ag(tripyridyl)X]^+$ (29)

d. $[Ag(o\text{-phenanthroline})_2]^{++}$. (30)(25)

e. $[Ag(picolinate)_2]$ Reddish brown. Isomorphous with the cupric salt (31), planar molecule (32)

f. $[Ag\ (quinolinate)_2]$ (33)

g. $[Ag\ (8\text{-hydroxyquinolate})_2]$ (34)
Prepared simply by adding 8-hydroxyquinoline to hot argentous acetate solution. Metallic silver separates as a mirror, and the green argentic compound precipitates

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(over)

P. Ray, Nature 151, 643 (1943) has obtained compounds of the type $[Ag(enBigH)_2]X_3$, where "enBigH" is ethylenebiguanide and X is nitrate, perchlorate, hydroxide, or sulfate. These are deep, permanganate red, and are quite stable at ordinary temperatures. The nitrate can be recrystallized from warm dilute nitric acid. The Ag^{+++} ion has the same configuration as Ni^{++}, and is accordingly diamagnetic. These salts liberate two equivalents of iodine from KI solution. Molecular conductivity of the nitrate at infinite dilution at 20° C is 455 $ohms^{-1}$ as would be expected of a salt of a tervalent ion.

FRACTIONAL SEPARATIONS

ILLUSTRATED BY SEPARATION OF RARE EARTHS

Howard E. Kremers March 7, 1944

I. Introduction

A. Methods available
B. Choosing the method
1. Since fractionation is a repitition of the same operation, the method should be simple, should not be susceptible to accidents, and should not result in a continual loss of material.
2. For inorganic materials, this generally leads to fractional crystallization as the best method.

II. Fractional Crystallization

A. In ordinary separations of substances, isomorphism is considered a hinderance. In fractionation, isomorphism is a necessity.
B. If the materials are not isomorphous, fractionation results only in the separation of the least soluble or most abundant constituent of a mixture.
C. Solubility differences are enhanced by the components of the mixture. For salts, the ions should be augmented as little as possible in order to promote greater solubility differences (4).
D. Method of fractional crystallization.
1. First stage: resolution of the mixture into fractions. The number of fractions increases with fractionation.
2. Second stage: the number of fractions remains the same.
E. Efficiency of fractionation is inversely proportional to the number of intermediate fractions.
1. Less soluble constituents of a mixture are usually more difficult to remove from the intermediate fractions than are more soluble constituents.
2. Changing the order of solubility helps in obtaining pure intermediate constituents.
3. "Separating elements" reduce the number of intermediate fractions and thereby promote efficiency.
a. Tl^+ in the separation of K^+ and Rb^+ alums.
b. Bi^{+++} in rare earth separations (5).
c. Use of rare earths themselves as separating elements in rare earth separations (6,7).

III. Technic of Fractional Separation.

A. "Separating elements" often aid in removing impurities from the soluble fractions.
B. In large-scale applications, the intermediate fractions of a long fractionated mixture may be added to the impure fractions of an initial separation thereby increasing the efficiency.

IV. References

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Some Compounds of Silicon

V. Boekelheide March 15, 1944

Silicon is directly below carbon in the periodic table, and for that reason, it would be expected that the behavior of silicon would be much like that of carbon. However, since silicon is below carbon, it would be expected also that silicon in contrast to carbon, would show a stronger affinity for negative non-metallic elements than for positive non-metallic elements. In this seminar an attempt will be made to show that both of these expectations have been justified experimentally.

Silicon Hydrides

Naming: SiH_4, silicane (silane); Si_2H_6 silicoethane (disilane); etc.

Preparation: $MgSi_2 + HCl \longrightarrow SiH_4 + Si_2H_6 + Si_3H_8 + Si_4H_{10} + Si_5H_{12} + Si_6H_{14} + MgCl_2 +$ silica

(Various silicon hydrides are separated by fractional distillation)

Properties: The hydrides are gases or low-boiling liquids, are soluble in non-polar solvents, and are extremely sensitive to air or moisture.

Reactions:

A. Combine explosively with oxygen or the halogens

B. React with halogen compounds to form silicon halides

$$SiH_4 + HCl \xrightarrow{AlCl_3} SiH_3Cl + H_2$$

$$Si_3H_8 + 4CHCl_3 \longrightarrow Si_3H_4Cl_4 + 4CH_2$$

C. React with alkali

$$Si_2H_6 + 4H_2O \xrightarrow{OH^-} 2SiO_2 + 7H_2$$

Alkyl and Aryl Derivatives

Preparation:

A. $SiH_3Cl + Zn(CH_3)_2 \longrightarrow SiH_3CH_3 + ZnCl_2$

B. $SiH_3Cl + RMgX \longrightarrow SiH_3R + MgX_2$

C. $SiCl_4 + RMgX \longrightarrow SiR_4 + R_3SiCl + R_2SiCl_2 + RSiCl_3$

D. $SiCl_4 + EtBr \xrightarrow{Na} SiEt_4 + NaBr + NaCl$

Reactions:

A. $CH_3SiH_3 + 2H_2O \longrightarrow [CH_3SiOOH]_x + 3H_2$

B. $CH_3SiH_2CH_3 + H_2O \longrightarrow (CH_3)_2SiO + 2H_2$

Silicon Halides

Preparation:

A. $SiO_2 + 2Cl_2 + 2C \xrightarrow{\Delta} SiCl_4 + 2CO$

B. $SiH_4 + HCl \xrightarrow{AlCl_3} SiH_3Cl + H_2$

Reactions:

A. Hydrolysis

B. With ammonia

$$3SiH_3Cl + 4NH_3 \longrightarrow (SiH_3)_3N + 3NH_4Cl$$

$$SiH_2Cl_2 + 3NH_3 \longrightarrow [SiH_2NH]_x + 2NH_4Cl$$

C. With alcohols

$$SiCl_4 + 4EtOH \longrightarrow Si(OEt)_4 + 4HCl$$

D. Wurtz, Grignard, and other such reactions.

Oxygen Derivatives

Preparation: Hydrolysis of silicon halides or hydrides.

Reactions:

A. $SiH_3(OH) \xrightarrow{\text{spontaneously}} (SiH_3)_2O + H_2O$

B. $R_2Si(OH)_2 \longrightarrow (R_2SiO)_X + H_2O$

$(R_2SiO)_X + R'MgX \longrightarrow R_2R'SiOH$

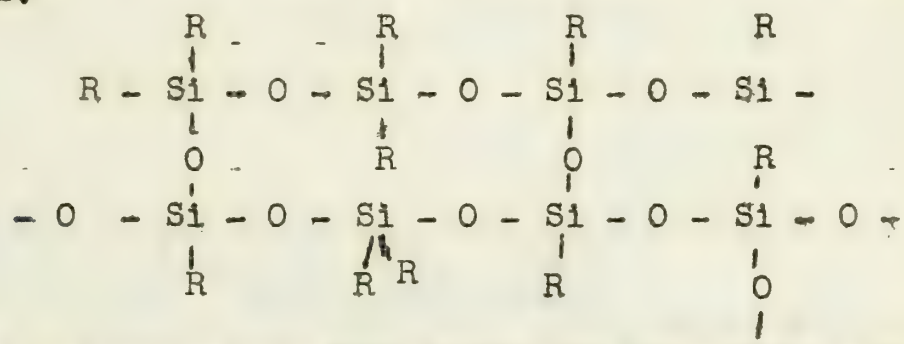
C. $RSi(OH)_3 \longrightarrow (RSiOOH)_X + H_2O$

Silicon Polymers

Preparation: $SiCl_4 + 4MgX \longrightarrow RSiCl_3 + R_2SiCl_2$

$RSiCl_3 + R_2SiCl_2 + H_2O \longrightarrow$ polymer

Structure: These polymers are evidently due to the formation of long chains of silicon to oxygen linkages. The $RSi(OH)_3$ is desirable because it cross-links these chains.



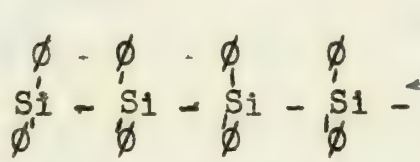
Properties: These polymers have the desirable properties of being extremely stable thermally and of having a low electrical conductivity. Samples of these polymers have been heated for a year in air at 200°C without appreciable decomposition.
Does not decompose at 550° in vacuo in 16 hours.

Organic Chemistry of Silicon

A. Wurtz reaction:

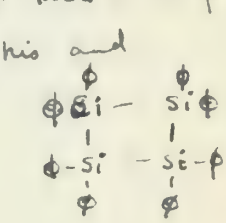
$\phi_2SiCl_2 + Na \longrightarrow Si_4\phi_8$

$Si_4\phi_8$ is probably



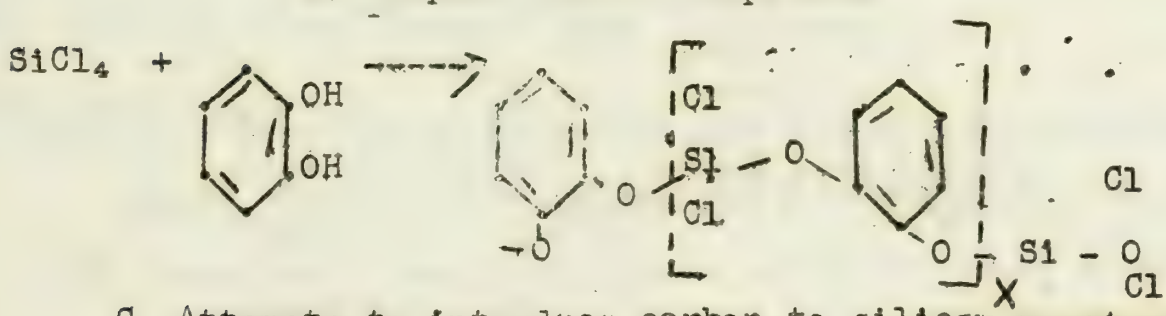
This exists in two forms

← This and



B. Reaction of $SiCl_4$ with alcohols and phenols

1. Ortho esters ($Si(OR)_4$).
2. Complex Phenol compounds



C. Attempts to introduce carbon to silicon ~~unsaturations~~.

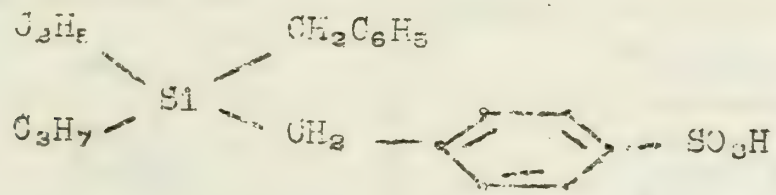
1. Dehydration of silicols.
2. Dehydrohalogenation of silicon halides. All attempts have been unsuccessful.

D. Orientation Studies

1. Nitration of tetraphenyl silicane gives substitution of the nitro group in the meta position predominatly, whereas phenyltriethyl silicane on nitration gives the para isomer.

E. Optically active silicon compounds

1. Challenger and Kipping have supposedly pre pared and resolved the tetrasubstituted silane below. Resolution was accomplished by recrystallization of the brucine salt.



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Oxyanions of Iron

James V. Quagliano March 28, 1944

Introduction:

A. Position of iron in periodic table and electronic configuration
B. Higher oxidation states of iron have been known for some time.(1)
C. "Ferrites" is general name given to class of compounds formed by reaction of ferric oxide with many bases.
D. Nomenclature of "ferrites."
   1. Literature and textbooks are not in agreement
   2. Suggested nomenclature (Mellor (1))

Oxidation No. of Iron	Anions	Names
+ II	$FeO_2^{=}$	hypoferrite
+ III	FeO_2^{-} $FeO_3^{\equiv}$ $Fe_2O_5^{==}$	(meta) ferrite (ortho) ferrite di ferrite
+IV	$FeO_3^{=}$ $Fe_2O_5^{=}$	perferrite diperferrite
+ VI	$FeO_4^{=}$	ferrate
+ VIII	$FeO_5^{=}$ (?)	per ferrate

Oxyanions of manganese can be named in similar fashion. (Manganese has same oxidation states -- with exception of max. of + VII)

Fe +II Hypoferrites

Electrolysis of a 40% NaOH solution using an iron anode in absence of air gives bluish green $Na_2FeO_2 \cdot 2H_2O$ (4)

Fe +III Ferrites

A. Magnetite, $Fe(FeO_2)_2$, franklinite, $(Fe,Mn,Zn)(FeO_2)_2$, chromite, $(Fe,Cr)((Cr,Fe)O_2)_2$ are commonly occurring minerals having analogous chemical composition and belong to Spinel Group.
B. General methods of preparation:
   1. Anodic oxidation of sodium hypoferrite solution or alkaline solution of ferrous hydroxide.(4)
   2. Heating to dryness of a solution of NaOH, $Co(NO_3)_2$ and $Fe(OH)_3$ and ignition of residue yields $Co(FeO_2)_2$ (3)
   3. Ignition of Cupric oxide and ferric oxide
   3. $Na_2CO_3 + Fe_2O_3 \longrightarrow 2NaFeO_2 + CO_2$ (17)
   4. $2NaOH + Fe_2O_3 \longrightarrow 2NaFeO_2 + H_2O$ (5)
   5. Heating hypoferrite solutions in presence of oxygen at 40-60°C
   6. Solid reaction between barium carbonate and ferric oxide. (18)

Fe +IV Perferrites

A. Preparation

1. Oxidation of ferrites by oxygen at high temperatures. (17)
2. Oxidation of mixture of barium and ferric hydroxides at 400°C. (8)
3. Li_2FeO_3, $SrFeO_3$, $BaFeO_3$ and Na_2FeO_3 can be prepared by oxidation of hydroxides with bromine or chlorine. (1)
4. Heating carbonates of Sr, Ba, Na, Li, with Fe_2O_3 in presence of oxygen. (1)
5. Heating of stoichiometrical mixtures $1CaO: 1Fe_2O_3$ and $1CaCO_3: 1Fe_2O_3$ in presence of air produces "active intermediates." (7)

B. Chemical Properites (2,3,4,11)

1. $4SrFeO_3 \rightleftharpoons 4SrO + 2Fe_2O_3 + O_2$
2. $4BaFeO_3 + 10H_2O \longrightarrow 4Ba(OH)_2 + 4Fe(OH)_3 + O_2$
3. $2SrFeO_3 + H_2O_2 + 4H_2O \longrightarrow 2Sr(OH)_2 + 2Fe(OH)_3 + O_2$
4. $4BaFeO_3 + 10H_2SO_4 \longrightarrow BaSO_4 + 2Fe_2(SO_4)_3 + 10H_2O + O_2$
   $2BaFeO_3 + 12HCl \longrightarrow 2BaCl_2 + 2FeCl_3 + Cl_2 + 6H_2O$
5. $4SrFeO_3 + 4CO_2 \longrightarrow 4SrCO_3 + 2Fe_2O_3 + O_2$

C. Uses of perferrites

Mixtures of air and alcohol or other inflammable vapors when led over heated perferrites are oxidized to carbon dioxide and water. Once the reaction has started, combustion proceeds of its own accord. The perferrites can be used as catalysts in such type reactions. (11)

Fe +VI Ferrates

A. Preparation:

1. Reaction of chlorine on ferric hydroxide suspended in potassium hydroxide yields ferrates (9,11). Chlorine may be replaced by ozone or sodium hypochlorite.
2. Electrolytic oxidation of ferrous and ferric salts. (12)
3. The ferrates of Zn(rose colored), Sr, (dark red), Cu(II) green, Al (rose - red), Cs(red), thorium (II), lead (II)(rose-colored), Cr(III)(yellow,) iron(II),(III), nickel (II) (gray-green), silver (black), have been prepared by treating suspension of barium ferrate with metal nitrate. (1)

B. Chemical reactions:

1. Hydrolysis of alkali ferrates (8)
2. $4Ag_2FeO_4 \longrightarrow 4Ag_2O + 2Fe_2O_3 + 3O_2$ (above 50°C). (10)
3. Reaction with acids. All acids, even carbonic, readily attack the ferrates -- when treated with HCl, chlorine is evolved.
4. Oxidation of organic substances. (11)
   Paper, wood and organic substances are slowly oxidized by a dilute solution of potassium ferrate. Alcohol is oxidized to aldelyde, tartrates and glycerol are readily oxidized, and also oxalates, urea and most soluble organic substances with the exception of acetates.

Fe +VIII Perferrates

D.K. Goralevich (16) states that bright green potassium perferrate, $K_2Fe_2O_5 \times H_2O$ is formed by fusion of ferric oxide with potassium hydroxide and excess $KClO_3$. $BaFeO_5 \cdot 7H_2O$ and $SiFeO_5 \cdot 7H_2O$ are obtained by treating suspension of potassium perferrate with alkaline earth salts. Schoelder (2) repeated the investigation of Goralevich

several times and in addition modified procedure but did not succeed in preparing a perferrate.

Investigation of ferrites and spirels by X-ray analysis, roentgenographic and magnetic methods (19,20)

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SELENIUM OXYCHLORIDE AS A SOLVENT

Marie B. Knobeloch

March 28, 1944

I. Introduction
   A. Historical development of acid-base theory. (1,2)
   B. Resulting theories
      1. Arrhenius Theory
      2. Theory of Solvent Systems
      3. Bronsted Theory
      4. Lewis Electron Theory
      5. Usanovich Theory

II. Solvent systems in general
   A. Characteristics
      1. Certain characteristic compounds, like H_2O, NH_3, SO_2, $COCl_2$, $SeOCl_2$, are parent compounds for a whole series of other materials.
      2. Parent compound must be able to undergo autoionization

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

   B. Strength of solvent system theory -- emphasis upon the fact that acid behavior is not confined to solutions containing proton donors.
   C. Weaknesses of theory
      1. Attempt to limit acid-base phenomena to solvent systems
      2. Undue emphasis upon ionization as the most important factor in acid-base properties
   D. Properties and reactions indicative of acid-base relations in a solvent. (2)
      1. Electrolytic solutions
      2. Well-defined acids, bases, and salts
      3. Neutralization reactions giving rise to salts and showing definite potentiometric endpoints
      4. Formation of solvates
   E. Classes of solvents considering acid-base reactions
      1. Inert toward acids and bases, e.g. benzene
      2. Ionizable, e.g., H_2O, $SeOCl_2$, NH_3
      3. Non-ionizable, e.g, ether, pyridine

III. Selenium oxychloride as a solvent
   A. Definitions according to G.B.L. Smith (3).
      1. Acid -- any solute whose molecule (neutral or charged) is an electron pair acceptor toward the molecule or an ion of the solvent.
      2. Base -- any solute whole molecule (neutral or charged) is an electron pair donor toward the molecule or an ion of the solvent.
   B. Relationship of the Smith theory to the Lewis Theory. (4)
   C. Ionization of $SeOCl_2$
      1. Expectation: $SeOCl_2 \rightleftharpoons SeO^{++} + 2Cl^-$ (5).
      2. Autoionization, $2SeOCl_2 \rightleftharpoons (SeOCl.SeOCl_2)^+ + Cl^-$, based upon following evidences: (3)
         a. Conductance of the pure liquid, 2×10^{-5} mhos. (6)
         b. Products formed when solutions are subjected to electrolysis

$SnCl_4 + SeOCl_2 \xrightarrow{e.c.} Cl_2 + Se_2Cl_2 + SeO_2$
(anode) (cathode)

$SnCl_4$ added to increase conductance of $SeOCl_2$

Anodic: $2Cl^- - 2e^- \longrightarrow Cl_2$

Cathodic: $6(SeOCl)^+ + 6e^- \longrightarrow 6SeOCl$

$6SeOCl \longrightarrow 2SeO_2 + Se_2Cl_2 + 8SeOCl_2$

$6(SeOCl \cdot SeOCl_2)^+ + 6e^- \longrightarrow 2SeO_2 + Se_2Cl_2 + 8SeOCl_2$

c. Products formed when a metal reacts with $SeOCl_2$

1. $3Cu + 4SeOCl_2 \longrightarrow 3CuCl_2 + Se_2Cl_2 + 2SeO_2$
   Explained by:

$3Cu + 6SeOCl^+ \longrightarrow 3Cu^{++} + Se_2Cl_2 + SeO_2 + 2SeOCl_2$

$3Cu^{++} + 6Cl^- \longrightarrow 3\ CuCl_2$

2. Action of $SeOCl_2$ on metals compared with action of $SeOCl_2 + SnCl_4$ on the same metals.

d. Composition of solvates of $SeOCl_2$, such as stannic chloride disolvate and pyridine monosolvate. (7) Electron pair acceptors (acids) $TiCl_4$, $SnCl_4$, $SO_3 \cdot SnCl_4 \cdot 2SeOCl_2$ $\xrightarrow{\text{auto-ionizes}}$ $(SeOCl)_2^{++}\ SnCl_6^{=}$; $(SeOCl)^+\ (SO_3Cl)^-$(8

Electron pair donors (bases) C_5H_5N, NH_3, etc. (11)

1. $C_5H_5N + SeOCl_2 \longrightarrow (C_5H_5NSeOCl)^+\ Cl^-$
2. $NH_3 + SeOCl_2 \longrightarrow NH_3SeOCl^+ + Cl^-$
   analogous to $NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$
3. $H_2O + SeOCl \cdot Cl \rightleftharpoons H_2SeO_2Cl_2$
   $H_2SeO_2Cl_2 \longrightarrow 2HCl + SeO_2$
4. Salts of strong metals and $SeOCl_2$. Chlorides of alkali and alkaline earth metals function as bases in $SeOCl_2$, and the molecule which is an electron pair donor is the charged molecule (the Cl^-)

e. The metathetical reactions which have been carried out in $SeOCl_2$ solutions.
$CaCl_2 + SnCl_4$ (precipitation) (9,3)

D. Conductance Titrations

1. Apparatus and procedure (10,3)
2. Individual titrations (resistance vs. ml. added)

a. pyridine with $SnCl_4$

$2(C_5H_5SeOCl)\ Cl + (SeOCl)_2\ (SnCl_6) \longrightarrow (C_5H_5NSeOCl)_2\ (SnCl_6) + 2SeOCl_2$

b. $SnCl_4$ with pyridine

c. KCl with $SnCl_4$ -- inflections in curve correspond to formation of $K(SeOCl)_3(SnCl_6)_2$ and $K(SeOCl)(SnCl_6)$

d. $SnCl_4$ with $CaCl_2$ -- 3 inflections due to $Ca[(SeOCl)SnCl_6]_2$, $CaSnCl_6$, $Ca_3(SnCl_7)_2$

e. $FeCl_3$ with pyridine -- 3 inflections due to formation of 1°, 2°, 3° salts:
$(C_5H_5NSeOCl)\ (SeOClFeCl_5)$, $(C_5H_5NSeOCl)_2\ (FeCl_5)$, and $(C_5H_5NSeOCl)_3\ (FeCl_6)$

f. SO_3 with pyridine -- 2 inflections due to $(C_5H_5NSeOCl)\ SO_3Cl$ and $(C_5H_5NSeOCl)_2\ SO_3Cl_2$

g. $AsCl_3$ with pyridine -- 3 inflection points:
$(C_5H_5NSeOCl)(SeOCl)(AsCl_4)_2$,
$(C_5H_5NSeOCl)(AsCl_4)$
$(C_5H_5NSeOCl)_2(AsCl_5)$ (3,7)

h. More recent conductance studies. (11,12,13)

E. Potentiometric Titrations (16) titrations

These were the first potentiometric titrations to be carried out in a non-protonic solvent; previous to this potentiometric titrations had been limited to protonic acids and bases and usually in protonic solvents. (14) Peterson, Heimerzheim, and Smith (13,15, 16,) obtained titration curves for neutralization reactions between non-protonic acids and non-protonic bases in the non-protonic solvent $SeOCl_2$.

1. Alkali and alkaline earth chlorides + SO_3 Overall equation:

$$K^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow SeOCl_2 + KSO_3Cl$$

2. Neutral molecule electron pair donors, isoquinoline, quinoline, and pyridine (bases)

$$C_5H_5NSeOCl^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow SeOCl_2 + C_5H_5NSeOCl^+ + SO_3Cl^-$$

or

$$C_5H_5NSeOCl^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow 2SeOCl_2 + C_5H_5NSO_3$$

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Divalent Rhodium and Its Complexes

R.W. Parry April 18, 1944

I. Introduction
- A. Position of rhodium in periodic table
- B. Reported oxidation states (1)
  1. Valences of 1,2,3 (most common), 4 (common in anions), 6.
  2. Valences 3,4, and 6 quite definitely established
     Valences 1 and 2 doubtful

II. Divalent Rhodium
- A. Reported occurrence

1. $4\ RhCl_3 \xrightarrow[960-70°C]{\Delta} 2\ RhCl_2 + 2RhCl + 3Cl_2$ (2)
2. $6\ Rh_2O_3 \xrightarrow[960°C]{\Delta} 4\ Rh_2O + 4\ RhO + 5O_2$ (2)
3. $Rh + Cl_2 \longrightarrow RhCl_2$ (3)
4. Complexes -- $Na_4\ [Rh(SO_3)_2 \cdot SO_4]$, $Na_6\ [Rh_2(SO_3)_4 \cdot SO_4]$
   $Na_2\ [Rh(SO_3)_2]$ (4)

- B. Existence of compounds in A questioned
  1. $RhCl_2$, Rh_2O, suggested as mixtures of Rh^{+++} and Rh metal. Analyses in every case not very good.
  2. Complexes probably sodium rhodic sulphites on basis of golden color of solutions. (5) Rhodous = red solutions.
- C. Work of Dwyer and Nyholm on reduction of Rh^{+++} with various reducing agents. (5) Distinguished five general classes of reducing agents.
  1. Yield metal only with no Rh^{++}
     (i.e. $CrCl_2$ in acid soln., NaH_2PO_2, formic acid, Cu,Sn,Pb)
  2. Yield chiefly metal but some evidence of Rh^{++} compounds
     (i.e. H_2SO_3, formic acid, Ag in presence of Br^-)
  3. Yield some metal but chiefly intensely red solutions of complex rhodous salts.
     (i.e. H_3PO_2 and $NaHSO_2$)
     $H_3PO_2 + 4RhCl_3 + 2H_2O \xrightarrow[\text{catalyst}]{Cu} H_3PO_4 + 4RhCl_2 + 4HCl$
  4. Yield Rh^{++} only but reaction rate very slow.
     (i.e. hydroxylamine hydrochloride or sulphate and similar salts of hydrazine)
  5. Yield no metal, only Rh^{++} -- reaction rate rapid
     (i.e. $SnCl_2$ and Na_2SnO_2)

(a) $Na_2SnO_2 + 2NaRhO_2 + 3H_2O \longrightarrow Na_2SnO_3 + 2NaOH + \underline{2Rh(OH)_2}$
ppt. contaminated with tin salts -

(b) Properties of impure rhodous salts prepared from $Rh(OH)_2$
$RhCl_2$ -- black, hygroscopic solid, hydrolyzed by H_2O, soluble in HCl to give red solution.
Rh^{++} oxidized to Rh^{+++} by O_2 of air, $HgCl_2$, H_2O_2, $KMnO_4$ in cold, and HNO_3 on warming

$$3\ Rh^{++} \xrightarrow[\text{inert atmos.}]{\text{Boiling}} 2\ Rh^{+++} + Rh$$

III. Complexes of divalent rhodium

A. Preparation of $RhCl_2 \cdot 3\ As\phi_2(CH_3)$ (6)

$RhCl_3 + 3\ As\phi_2(CH_3) \longrightarrow RhCl_3 \cdot 3AsR_3$ $R = \phi$ or CH_3

$4\ RhCl_3 \cdot 3AsR_3 + H_3PO_2 \xrightarrow[\text{acid}]{\text{strongly}} 2[RhCl_2 \cdot 3AsR_3]_2 + H_3PO_4 + 4HCl$

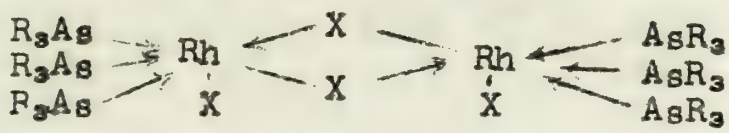
Complexes of Br and I also reported

Complexes of $As\phi(CH_3)_2$ also reported (8)

B. Properties of complex

1. brown to red crystalline solid; sharp m.p. at 171°C
2. liquid breaks down ----> arsine + Rh metal
3. insoluble in ionizing solvents as H_2O and EtOH
4. yields no ppt. of Ag halide on treatment with Ag^+
5. soluble benzene and chloroform
6. dimeric in boiling chloroform
7. powerful reducing agents
8. analysis very close to the theoretical

C. Proposed structure (6) with halogen bridges analogous to Al_2Cl_6 $[CuI \cdot 2PR_3]_2$ and $[PdCl_2 \cdot PR_3]_2$



all bonds covalent on basis of properties (6)

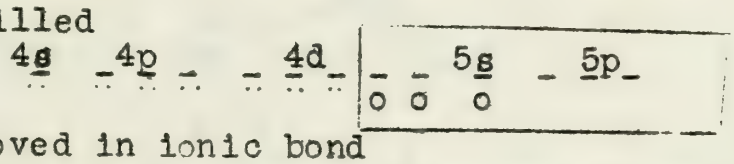
IV. Theoretical treatment of structures of Rh complexes

A. Orbital types (10)

1. $s^1p^3d^3$ ----> regular octahedron. Strength 2.923
2. $s^1p^3d^2$ ----> 4 planar and one weak p bond, strength 2.694
3. s^1p^3 ----> tetrahedron as in C. Strength = 2.0

B. Trivalent Rh structure

Lower orbitals filled



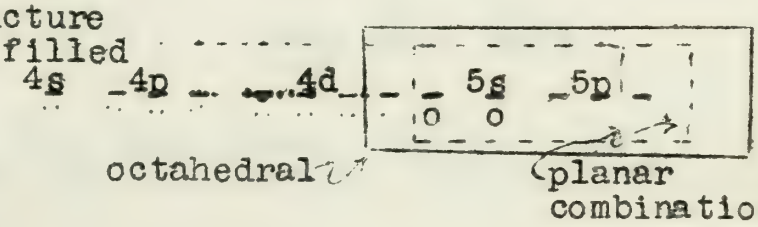
o = electron removed in ionic bond

$s^1p^3d^2$ available to give octahedron; agreement with fact excellent

C. Divalent Rh structure

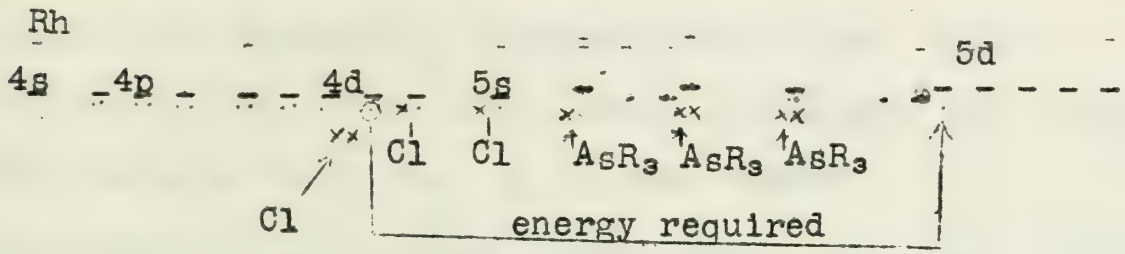
1. Electronic structure

Lower orbitals filled



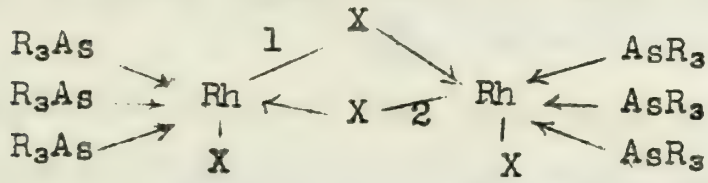
2. Planar combination
   a. bonds weaker than in octahedron (i.e. 2.694 compared to 2.923)
   b. present evidence indicates no square configuration of Rh^{++} (7)
3. Octahedral combination

a. Electronic representation involving halogen bridge of Dwyer and Nyholm (6) (all bonds covalent)

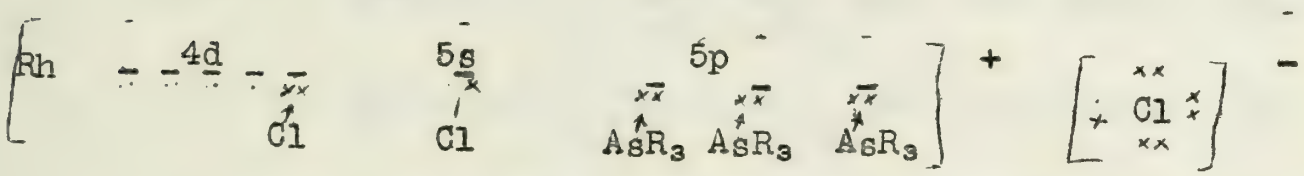


If all covalent, properties would be:
1. paramagnetic = to 2 unpaired electrons
2. less stable than Rh^{++} (analogous case of $[Co(CN)_6]^{-4}$

b. Halogen bridge with two bonds largely ionic

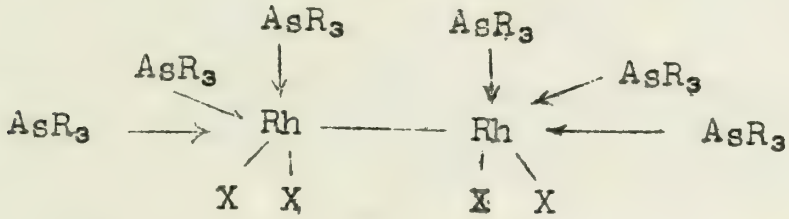


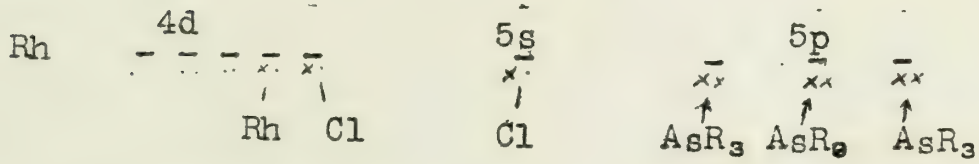
bonds 1 and 2 ionic



objections -- properties and theoretical treatment

c. Covalent Rh-Rh bond





Properties:
1. Weak Rh-Rh bond make strong reducing agent
2. More stable than Rh^{++} because orbitals of equal energy full
3. Diamagnetic
4. Octohedral bonds about Rh according to theory

d. Differences between rhodous complexes and cases of Al_2Cl_6 and $[CuI\ (PR_3)_2]_2$ cited as analogous
   1. stabilizing effects of chelation in these molecules

e. Question can be settled by magnetic measurements

V. Other rhodous complexes (8)(9)

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10. Pauling -- Nature of the Chemical Bond (1940)

ULTRASONICS

A.L. Oppegard

April 25, 1944

I. Introduction
   A. Historical
      1. Used in World War I, U-boats
      2. Developed in England for sounding purposes
      3. Discovery of biological effects
   B. Comparison of audible sound and ultra-sonic waves. (19)
      1. Wave lengths
         a. audible range is ten octaves, up to 20,000 vib./sec.
         b. ultrasonics -- 20,000 to 500 million vib/sec
            15 octaves about the audible range.
      2. Energies
         a. ordinary sound 10^{-9} watts/cc
         b. cannot shot 10^{-3} watts/cc
         c. ultrasonic waves 10 watts/cc
         d. frequency not as important as the intensity

II. Methods of production
   A. Historical
      1. Obtained very high frequencies by passing air through a high frequency resonator.
      2. Of little use since there is 99% reflection on going from a gas to a liquid or solid.
   B. Modern methods (19)
      1. Piezo electricity
         High frequency current applied to a quartz plate causes it to vibrate at its natural frequency giving rise to ultrasonic waves of high frequency and intensity. The unit is immersed in transformer oil.
      2. Magnetostriction
         A nickel or steel bar which is in an alternating magnetic field will vibrate at a very high frequency. This is the best for technical applications.

III. Effects of ultrasonic radiation
   A. Cavitation
      The formation and sudden and violent collapse of small bubbles of gas which appear on the radiation of liquids containing dissolved gases.
   B. Oxidations (1)(6)(7)(11)(13)(14)(20)(21)(3)
      1. There are several theories. The generally accepted one states that the dissolved oxygen is first activated, may then form hydrogen peroxide or oxidize other substances. If nitrogen is also present, nitrous and nitric acids may be formed.
      2. The activation of oxygen is accompanied by luminescence.
      3. Reactions
         a. halides to free halogens
         b. organic halides to the free halogen
         c. hydrogen sulfide to free sulfur
         d. sodium sulfite to sodium sulfate
         e. luminol
         f. bromthymol blue (18)

C. Emulsions (19)(22)
   1. Metals in liquids
      a. theory
      b. examples, Hg in water
   2. Liquids in liquids
      a. theory -- cavitation
      b. examples -- benzene in water
   3. Vaporization
   4. Finer photographic emulsions

D. Electrode potentials and passivity (2)(15)
   1. Depolarization, shift of potential
   2. Passivity destroyed
      a. depolarization
      b. disperse protective coating

E. Displacement of metastable equilibrium (18)
   1. Discharge nitrogen tri-iodide
   2. Yellow mercuric iodide to the red form below 120°
   3. Relieves superheating

F. Acceleration of reactions (4)(10)(18)(20)
   Direction is never changed, only the rate
   1. Hydrolysis of methyl sulfate is unaffected
   2. Polymerizations (also depolymerizations)
   3. Iodine clock reaction accelerated
   4. Hydrolysis of $K_2S_2O_8$ (23).

G. Metallurgy (8)(19)
   1. Gives a finer and more uniform structure to alloys and pure metals
   2. Also used in locating faults

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COLOR AND ITS RELATION TO INORGANIC STRUCTURES

J.A. Mattern

May 9, 1944

I. The nature of color
   A. Color results whenever a substance absorbs light unequally in the visible region
   B. The colors of the spectrum and characteristic wave lengths
   C. Complementary colors -- the relation of absorption curve to color transmitted

II. The measurement of color
   A. Method of extinction
      1. Pass white light through a solution and then through a spectroscope
      2. Dilute or use thinner cell until bands disappear
      3. Use of the gradient wedge
   B. The spectrophotometer
      1. Use of a divided light beam
      2. Reduce intensity of "standard" beam and compare with that through solution
      3. Methods of recording data
   C. The plotting of absorption curves
      1. Beer's law
      2. Lambert's law
      3. Extinction coefficient
      4. Absorption coefficient

III. Color theory from the historical standpoint
   A. Development slow because of the lack of an adequate theory of atomic and molecular structure
      1. Organic vs inorganic viewpoints
         (a) Color of organic compounds regarded as a molecular phenomenon and of inorganic compounds as an atomic process
         (b) Lack of color in most compounds of carbon, hydrogen, oxygen, nitrogen, etc.
         (c) However structure plays an important role in inorganic colors as well
   B. Early viewpoints
      1. The concept of the vibrating atom or group
      2. The concept of the vibrating electron
   C. Foundations for the modern viewpoint
      1. Lewis (1916) -- the electron with constrained vibrations (6)
      2. Lewis (1923) -- the electron with constrained energy states (7)
      3. Bichowsky (1918) -- variable valence (2)
      4. Fajans (1923) -- deformation of anions (4)
      5. Stieglitz (1923) -- oxidation and reduction (12)
      6. Yntema (1926) -- incomplete electron shells (16)
      7. Pitzer and Hildebrand (1941) -- covalent character (10)

IV. The nature of the absorption process
- A. General absorption
- B. Characteristic absorption
  1. Rotation--far infrared
  2. Vibration--infrared
  3. Electronic--visible or ultraviolet
- C. The "continuous" nature of absorption curves (2)
  1. The Stark effect
  2. Rotation and vibration
- D. Effect of physical state upon color
  1. Color of solids a function of crystal structure and particle size
  2. Effect of temperature upon crystalline solids (1)
  3. Variation of solvent (14)

V. The color of coordination compounds (3,5,8,9,11,13,15)
- A. The three absorption bands
  1. First band -- transition elements
  2. Second band -- coordination groups
  3. Third band -- negative groups trans to each other
- B. Relation of color to stability

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- A. General references

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Energy Relationships in Inorganic Chemistry

H.A. Laitinen

May 16, 1944

I. Usefulness of energy concept -- kinetics vs. thermodynamics.
   A. Free energy determines completeness of reactions; stability of compounds.
   B. Heat of reaction as semiquantitative approximation.

II. The Born-Haber cycle, definition of energy terms.
   A. Crystal energy, ionization potential, electron affinity, sublimation energy, dissociation energy, heat of formation.
   B. Application of Born-Haber cycle to determine electron affinity or crystal energy.

III. Stability of ionic compounds
   A. NaCl -- Formation of gaseous ions from elements is an endothermic process. Crystal energy responsible for stability.
   B. CaO -- Ions even more endothermic than for NaCl, but crystal energy much larger.
   C. SrO -- less stable than CaO in spite of more active metal because of smaller crystal energy.
   D. HgO -- less stable because of higher ionization potential.
   E. Alkali metal hydrides -- LiH most stable.

IV. Partial covalent character of crystals.
   A. Comparison of experimental and calculated crystal energies for CuI, difference represents covalent character.
   B. Results:
      1. Fluorides, oxides mainly ionic
      2. Decreasing ionic character in series AgF, AgCl, AgBr, AgI

V. Solubility of salts
   A. Energy of hydration -- relation to ionic size and charge
   B. Comparison of AgCl and AgF, effect of covalent character
   C. Consideration of entropy change, comparison of LiF and other alkali halides.

VI. Activity of metals
   A. Effect of sublimation energy, ionization potential and hydration energies; comparison of Na and Ag.

VII. Strength of acids in aqueous solution (5)
   A. Energy and entropy of transfer of proton
   B. Energy and entropy of hydration
   C. Calculation of ionization constant

VIII. Strength of oxidizing agents
   A. Comparison of strengths of ClO_3^-, BrO_3^-, and IO_3^- as oxidizing agents shows IO_3^- in solution to be abnormally stable, probably because of higher hydration.

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Alloys, Their History and Relation to the History of Chemistry

Virginia Bartow

May 23, 1944

I. Introduction
   1. Historical periods in chemistry -- ancient, alchemical iatrochemical, phlogiston and modern.
   2. Historical periods for alloys -- early and modern
   3. Derivation of the word alloy

II. Early period
   1. Mining and metallurgy of metals and alloys
      a. Order of production -- Au, Cu, Au-Cu, Cu-Sn, Cu-Zn, Fe, Pb, Ag, Au-Ag, Sb, Hg
      b. Myths -- the forest fire, lightning, gods and kings as the important influence in production
      c. Production of bronze as hardened copper
         1. Derivation of names from Cyprus and Brundisium. Brass and bronze interchangeable. An asiatic discovery
         2. Ancient records -- Tubal Cain, Solomon, Herod, Rhodes
         3. Theory of sources of bronze
            a. Cu-Sn ore
            b. Cu ore and Sn
            c. Cu and Sn
            d. Cu ore and Sn ore. Location of the Sn ore, the "diabolous metallorum", Khorassan and Britain.
         4. Bronze production in Egypt as hard as steel disproved
      d. Production of iron
         1. Origin uncertain
         2. A tribute to the great rulers and a foreign metal for years
      e. Production of asem and electrum -- the gold-silver alloys of Egypt.
         1. Developed by priests and artisans
         2. Receipes in papyrus records.
         3. Assaying developed to detect the alloys.
   2. Influence on chemical history
      a. Forerunner of alchemy which with the Greek philosophy of the unity of matter and medieval metallurgy laid the foundations of modern chemistry
      b. Books -- "Probierbüchlein", "Pyrotechnia" of Biringuccio and "De Re Metallica" of Agricola early products of the printing press. These are the earliest examples of authentic, accurate scientific writing.

III. Modern Period
   1. 18th century
      a. Six or seven metals in use and ten others known.
      b. Alloys restricted to brass, bronze, gun metal, bell metal, pewter.
      c. Beginning of the period of discovery of new elements
   2. First half of the 19th century
      a. Systematic study of alloys by Michael Faraday
      b. No new alloys mentioned in J.W. Draper's text, 1846
      c. Berthellot: Equilibrium and Law of Mass Action

3. Second half of the 19th century
   a. Alloys in Instruments -- balance, weights, autoclave, clocks marine chronometers, "fire engines".
   b. Early scientific study of alloys
      1. Microscopic work -- Hooke, Reaumuh, Grignon, Widmanstätter
      2. The Photomicrograph -- Sorby 1863
      3. Study of properties dependent on crystal structure
         a. Thermal conductivity
         b. Electrical conductivity
         c. Diffusion
         d. Thermal equilibrium diagrams
         e. Magnetic properties
         f. Later -- X-rays
      4. Intermetallic compounds in alloys
         a. Relation to modern molecular structure
   c. Alloys in applied chemistry
      1. Production of iron
      2. Alloy steels -- manganese, high speed steels, molybdenum
      3. Special alloys -- as permalloy, nichrome, ligh alloys
      4. Water purification
      5. Haber process

IV. Conclusion
   1. Haber's three stages in modern chemistry related to alloys
      a. Synthetic
      b. Thermodynamic
      c. Atomic structure

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107 Chemistry Annex
November 5, 1944

Dear Friends:

This letter is being sent to all alumni of the Chemistry Department whom we think may be interested in receiving outlines of the talks in our regular weekly INORGANIC SEMINAR. A sample copy is enclosed, so that you may see whether such outlines will be of value to you. For the present, at least, no charge will be made for the outlines. If, in future years, the subscription list becomes so great that it burdens our postage fund, we may have to charge enough to cover the cost of paper, envelopes and postage. We shall be happy to send the outlines to anyone who is really interested in them and will find them useful. If you wish to have your name on the mailing list, please let me know. The outlines will be sent out about once a month.

The pages will be numbered consecutively starting at the beginning of each school year, and a Table of Contents will be sent to each subscriber at the end of the year. It is hoped that some of you, at least, will wish to preserve the outlines in bound form or in loose leaf books.

While these outlines are prepared primarily for the use of the members of the seminar class, we hope they will be of service also to others. To that end, we shall welcome suggestions as to topics, mode of presentation, etc. We shall try to follow these suggestions insofar as they fit into our seminar plans.

A few copies of the outlines for the past three years are available, and will be distributed as long as they last.

University enrollment this fall is about 6000 -- more than last year, but still low. In addition, we have about 400 men in the Navy V-12 and about 500 ASTRP men. Most of the students in the military training programs are enrolled in general chemistry, so we on the staff are kept very busy. It is extremely difficult to find teachers, but we are getting along this fall by using a couple of seniors and by overcrowding the classes.

Plans for a new Chemistry Building are again active, and we hope that the legislature will grant funds for it as soon as the war is over.

Sincerely yours,

John C. Bailar Jr.

John C. Bailar, Jr.
Professor of Chemistry
Department Secretary

JCB/pf

THE COORDINATION NUMBER OF COPPER IN THE POLYETHYLENE-AMMONIUM CHLOROCUPROATES

Hans Jonassen October 24, 1944

Coordination numbers from one to six have been reported for the coordination of chloride ions to the central copper ion in the presence of excess chloride ions.

In the study of absorption spectra of copper chloride solutions, Getman (1) reported in 1922 that in solutions containing copper and chloride ions the displacement of the region of maximum transmittency toward longer wave-length with increasing chloride ion concentration was due to the displacement of the equilibrium:

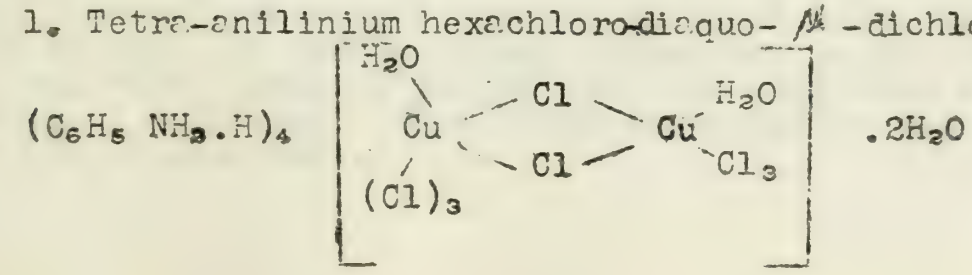
$$Cu(H_2O)_4^{+2} + 4Cl^- \rightleftharpoons CuCl_4^{-2} + 4H_2O$$

Spacu and Murgulescu (2) reached similar conclusions from spectrophotometric studies of the system. They postulated the formation of both $CuCl_4^=$ and $CuCl_3^-$ complexes in such solutions. Babko(3) obtained data which indicated the presence of the following chlorocuproates in such solutions: $CuCl^+$, $CuCl_3^-$, $CuCl_4^=$. Bhagwat (4) ascribed the inapplicability of Beer's Law to copper chloride solutions to the presence of such complex ions as $CuCl^+$, $CuCl_3^-$, $CuCl_4^=$, as well as the Cu^{+2} ion itself. Moeller (5), applying a modification of Job's method of continuous variation to a solution of copper containing excess chloride ions, obtained data which seemed to prove definitely the presence of $CuCl_4^=$ ions in the solution, but his data do not preclude the existence of any other chlorocuproates. All the data cited above seem to indicate that the colors of the $CuCl_4^=$ and $CuCl_3^-$ are yellow rather than blue.

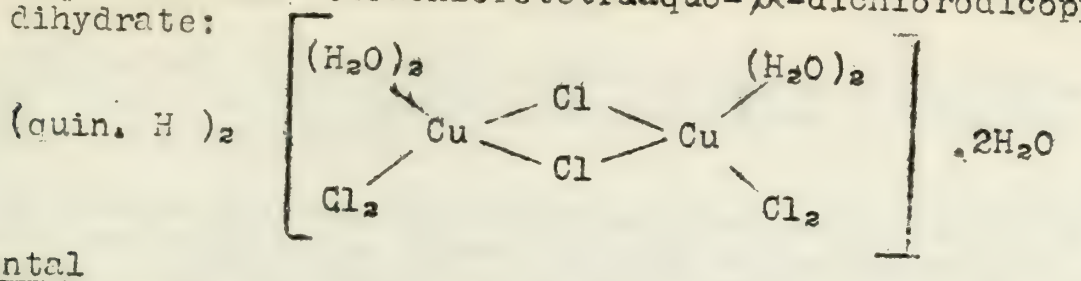
Similar complexes also have been prepared in the crystalline state. Topsoe (7) reported the preparation of yellow chlorocuproates of methylamine, dimethylamine and trimethylamine. In 1906, Grossman and Schuack (8) prepared the tetrachlorocuproate of ethylenediamine. The series of chlorocuproates of organic substitued monoamines was extended by Remy and Laves (9), Dehn (10), Michaelenko (11), and Amiel (12, 13). The chlorocuproates isolated by these authors contained $CuCl_3^-$, $CuCl_4^=$ complexes. The structures assigned to these indicated mononuclear complex ions, giving copper and coordination numbers of three, four, and five respectively.

In 1936 Dubsky and Wagenhofer (14) postulated a new theory. They maintained that all chlorocuproates prepared up to that time were really hexachlorocuproates of polynuclear structure containing two or more chloride bridges. They prepared a series of hexachlorocuproates to substantiate their theory. Two of the compounds prepared by them with the structures which they postulated are given below.

1. Tetra-anilinium hexachloro-diaquo-μ-dichlorodicopper dihydrate



2. Diquinolinium tetrachlorotetraaquo-μ-dichlorodicopper dihydrate:



Experimental

The research project started as an investigation of the complexes formed between copper and the straight chain polyethylene bases of the Hofmann series: diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The complexes formed between an aqueous solution of copper sulfate and the amines could not be precipitated by the addition of an organic solvent nor by evaporation. Similar results were obtained with aqueous solutions of copper chloride; but when $CuCl_2 . 2H_2O$ was dissolved in methanol and the amine was added to this solution a precipitate was formed. The first precipitate formed had a yellow color, but upon stirring and further addition of amine the solution solidified forming a green meal. After filtering, the green meal showed the presence of several solid phases: a yellowish green phase, a deep green phase, and a deep blue phase on the top layer. The blue phase of the top layer seemed to be a hydration product of the other two phases. Excess amine was added to part of the precipitate and it dissolved forming a deep blue solution. Concentrated hydrochloric acid was added to the remainder and a yellow precipitate was formed which was very soluble in water but which could be reprecipitated by the addition of an equal amount of concentrated hydrochloric acid. All the polyethylene amines gave similar yellow precipitates when prepared in a similar fashion.

Analysis showed that the following empirical formulae could be assigned to the compounds:

1. The diethylenetriamine complex: $NH_2C_2H_4NHC_2H_4NH_2 . 3HCl . CuCl_2$
2. The triethylenetetramine complex: $NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2 . 4HCl, CuCl_2$
3. No reasonable empirical formula could be calculated for the tetraethylenepentamine complex with copper ion.

The first member of this series, the ethylenediamine complex, which had been obtained previously by Grossman and Schueck (8), was also prepared in order to compare its physical and chemical properties with those of the higher members of this series. Analysis showed it to have the following composition: $NH_2C_2H_4NH_2 . 2HCl . CuCl_2$

Discussion of Results:

Microscopic investigation showed that the en(ethylenediamine), dien(diethylenetriamine), and the trien(triethylenetetramine) complexes were translucent, showed birefringency, and had well defined crystalline configurations; whereas the tetren(tetraethylenepentamine) complex formed ill-defined opaque crystal clusters with only slight birefringency on the corners of the crystals. Molecular weight determinations by freezing point lowering showed that the complexes dissociated completely in aqueous solutions. This total dissociation was further substantiated by the following facts:

1. All the chloride present in the complex precipitated immediately, and only a short digestion was necessary to coagulate the silver chloride precipitate.

2. It proved possible to determine the total acidity of the aqueous solution of the complex by titration with sodium hydroxide. This would seem possible, only if the amine hydrochloride existed as such in the solution.

3. The blue color of the aqueous solution of the complex agreed both in color and in hue with an aqueous solution of copper ions of equivalent concentration.

4. Magnetic susceptibility measurements made by Amiel (15) on similar chlorocuprates showed that even in the solid state the magnetic properties of the copper in chlorocuprates are the same as those of the hydrated copper ion.

All of these facts seem then to point to the following conclusions:

1. The complexes dissociate completely in aqueous solutions.
2. Complete dissociation can only be explained if it is assumed that the complexes in the solid phase are linked by ion-dipole attraction.
3. With ion-dipole attraction only mononuclear chloro complex configurations would seem reasonable.
4. With mononuclear configuration the central copper ion seems to have a coordination number of four for the ethylenediammonium tetrachlorocuprate, of five for the diethylenetriammonium pentachlorocuprate, and of six for triethylenetetrammonium hexachlorocuprate.
5. Since these complexes dissociate completely in aqueous solution they can be said to exist as such only in the solid state; and in the solid state are obtained most easily in the presence of a high concentration of hydrochloric acid.

From these conclusions, the following structures have been tentatively assigned to these complexes.

1. En complex: $en.H_2$ $\left[\begin{matrix} Cl & & Cl \\ & Cu & \\ Cl & & Cl \end{matrix}\right]$

2. Dien complex: $dien.H_3$ $\left[\begin{matrix} Cl & & Cl \\ Cl & Cu & \\ Cl & & Cl \end{matrix}\right]$

3. Trien complex: $trien.H_4$ $\left[\begin{matrix} Cl & & Cl \\ Cl & Cu & Cl \\ Cl & & Cl \end{matrix}\right]$

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ROLL CALL

October 24, 1944

Ionization in Methanol

W. E. Morrell

By colorimetric (indicator) and conductimetric methods, Guss and Kolthoff (J.A.C.S., 66, 1484-88 (1944)) studied the behavior of SO_2 in methanol. They conclude that $CH_3-O-\underset{\underset{O}{\|}}{S}-O-H$ (cf. $H-O-\underset{\underset{O}{\|}}{S}-O-H$) is formed, and that its dissociation constant in methanol is 3×10^{-7}.

$$CH_3OH + SO_2 = CH_3OSO_2H = CH_3OSO_2^- + CH_3OH_2^+$$

$$\frac{a_{CH_3OSO_2^-} \cdot a_{CH_3OH_2^+}}{a_{SO_2}} = K_A = 3 \times 10^{-7}$$

(The constant for the corresponding dissociation in water is 2×10^{-2}.)

The authors state that they find no indication of SO_2 acting as a "Lewis" acid with their indicator, thymol blue.

The addition of small quantities of water to methanol solutions of SO_2 results in the transfer of protons from methanolium ions to water, the water acting as a Bronsted "base".

Kanning, Byrne and Bobalek (J.A.C.S., 66, 1700-03 (1944)) (cf. ibid., 65, 1111-16 (1943)) studied the conductivity of sulfuric acid in methanol, and from their data calculated the dissociation constant of sulfuric acid in methanol. They report the following values:

t, ° C.	K
20	0.027
25	0.024
30	0.024
35	0.018

Although they list two significant figures in the values of the constant at various temperatures, the authors state that the techniques employed can yield only orders of magnitude.

The authors conclude that sulfuric acid in methanol exhibits properties of a strong univalent electrolyte.

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Spectrophotometric Estimation of Certain Rare Earth Elements

Therald Moeller

Aqueous solutions of salts of many of the rare earth elements are characterized not only by their very definite absorption spectra but also by the sharpness and intensities of many of the absorption bands in both the visible and infra red regions. A comprehensive spectrophotometric examination of aqueous solutions of the nitrates of most of the rare earth elements (including yttrium) in the spectral range 350 to 100 mμ has been published by Rodden (1,2). Inasmuch as the positions of the absorption bands differ among the various elements and inasmuch as most of the systems obey the Beers relation fairly well, a quantitative method of estimating one material in the presence of others is available. This is particularly true for the determination of a colored substance in the presence of a colorless one such as lanthanum, gadolinium, terbium, yttrium , ytterbium (in the visible), and lutecium, since solutions of the nitrates of these elements show no absorption. The determination of colored components in the presence of each other is easily done if all others exhibit 100% transmittancy at the wave length where one absorbs or if corrections are made by determining the absorptions of all others as pure substances at that desired wave length.

Applications. -- Rodden (1, 2) lists a number of analyses of mixtures, especially of the cerium earths. In brief, the method consists in reducing cerium-free oxides with hydrogen (to convert Pr_6O_{11} to Pr_2O_3) and examining a nitrate solution at 402 mμ (Sm), 446 mμ(Pr), and 521 mμ (Nd). A slight correction for the interference of Sm with the Pr analysis is then made and lanthanum is obtained by difference. This method has been successfully applied in this laboratory through use of General Electric Recording Spectrophotometer (3).

Among the yttrium earths, the chief utility appears to lie in a quantitative following of a fractionation procedure or in the estimation of a colored component in the presence of yttrium. In this laboratory, the ferrocyanide separation of yttrium from erbium (4,5) and the sulfate fractionation of the yttrium earths (4) have been followed, and quantitative analyses of erbium, thulium, and ytterbium samples have been made with excellent and rapidly attainable results.

The effects of certain anions upon these absorption spectra appear to be very pronounced (6); so a standard procedure is necessary.

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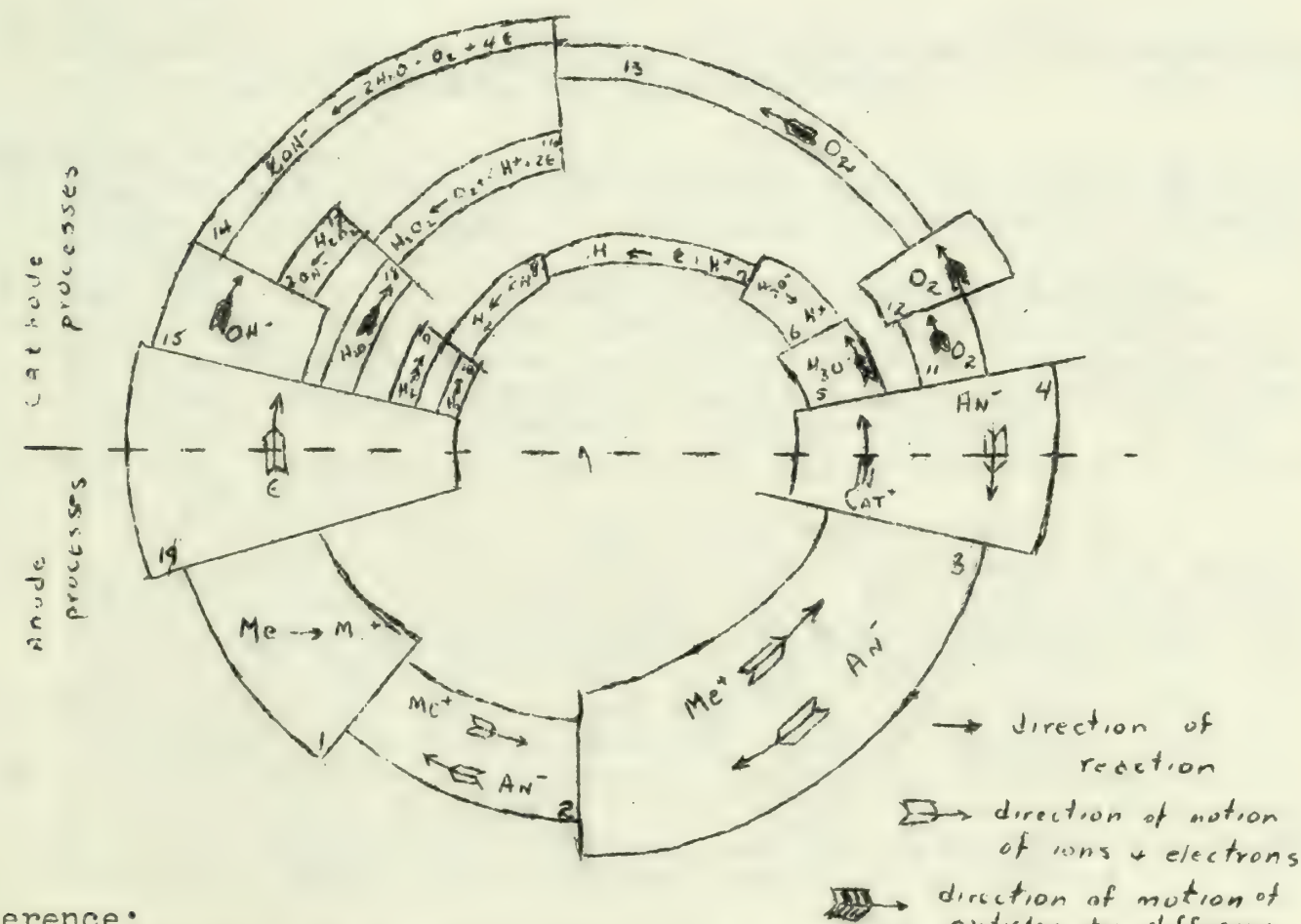
Diagram of the Corrosion Process

Clifford R. Keizer

1. Ionization of the metal: $Me \longrightarrow Me^+ + e$
2. Passage of metal ions along flaws on surface of metal into solution or of ions in solution in the reverse direction.
3. Removal of metal ions from the surface of the anode by their diffusion into the body of the solution.
4. Motion of the ions in solution under the influence of the electric poles.
5. Diffusion of hydrated hydrogen ions (H_3O^+) toward cathode.
6. Dehydration of H_3O^+.
7. Process of neutralization of hydrogen ions $H^+ + e^- \longrightarrow H$
8. "Malization" of hydrogen atoms $2H \longrightarrow H_2$
9. Diffusion of the hydrogen molecules toward the cathode.
10. Formation of hydrogen bubbles and their release at the surface of the cathode.
11. Passage of oxygen from the air to the electrolyte.
12. Passage of oxygen through the solution by convection.
13. Diffusion of oxygen along the electrolyte layer adjoining the cathode.
14. Reduction of oxygen at the surface of the cathode forming OH^-
$$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$$
15. Diffusion of OH^- ions from the cathode.
16. Process of reduction of oxygen to hydrogen peroxide
$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$$
17. Process of further reduction of hydrogen peroxide to OH^-
$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$
18. Diffusion of reduced H_2O_2 ($6OH^-$) from the cathode.
19. Flow of electrons in the metal.



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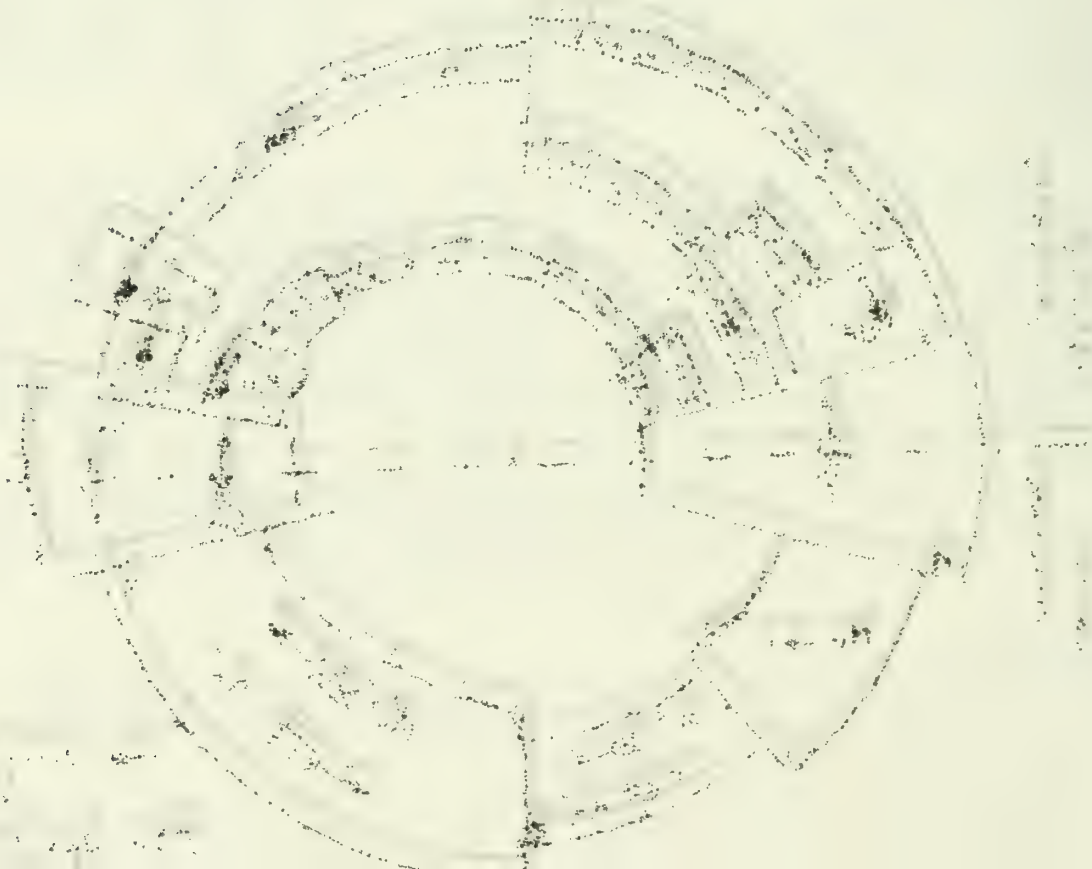

OXIDATION STATES OF COBALT AND NICKEL

John C. Bailar, Jr. November 7, 1944

I. Introduction

A. Methods of Determining Oxidation State

1. Analysis of Compounds. This is misleading unless the structure of the compound is known. Thus, $NiO_2.xH_2O$ exists in two forms -- dioxide and peroxide. The former is black, and contains tetravalent nickel; the latter is green, and contains divalent nickel. It is obtained by the action of H_2O_2 on Ni^{++}, and liberates H_2O_2 when treated with acids. It has never been obtained pure, the Ni:O ratio varying from 1:1.49 to 1:1.98. (1) CoS_2 and NiS_2 do not contain tetravalent metal, but have been shown magnetically to contain divalent metal. (2) They are analagous to pyrite. (3)
2. Properties of the ion in question -- most cobaltic and nickelic compounds are oxidizing agents.
3. Isomorphism with compounds of known oxidation state.
4. Physical methods, such as magnetic susceptibility.

II. Zero-valent and negative valent metals.

A. The carbonyls, nitrosyls, and carbonyl hydrides. If we assume that the electrons in $Ni(CO)_4$ belong to the CO molecules, Ni is zerovalent. If the electrons are partially controlled by the metal, Ni has a negative valence.
Blanchard (4) assumes that in dimeric carbonyls the metal is negative. He believes that an electron is transferred from NO to Co in such compounds as $Co(CO)_3NO$, and from H to Co in $Co(CO)_4H$.

B. Cyanides.
Burgess (5) reduced $K_2Ni(CN)_4$ with potassium in liquid ammonia, and obtained $K_4Ni(CN)_4$ as yellow crystals.

III. Monovalent Metals.

A. Ni_2O has been reported, but probably does not exist. X-ray diagrams indicate only the existence of mixtures of NiO and Ni (14).

B. $K_2Ni(CN)_4$ is reduced by many reducing agents to $K_2Ni(CN)_3$. Alkali metal amalgams are probably best (6,7,8) but zinc, $SnCl_2$ and NaH_2PO_2 can be used. Electrolytic methods are also suitable. $K_2Ni(CN)_3$ readily absorbs O_2 from the air, and in the absence of air, liberates hydrogen from water. In the absence of excess KCN, however, it may be preserved for several days. (8a,8c,9)

$$4K_2Ni(CN)_3 + 2H_2O \text{ --- } 3K_2Ni(CN)_4 + Ni + 2KOH + H_2$$

The oxidation-reduction potential has been measured by Grube and Lieder (10) and by Tedeschi (11). $E^\circ = 0.82$ volts. It reduces $KMnO_4$, $K_2Cr_2O_7$, H_2O_2(6) and I_2(6) quantitatively. It reduces Ag^+, Hg^{++}, Pb^{++}, Bi^{+++}, As^{+3} to metal. (6)

C. Acidification of solutions of $K_2Ni(CN)_3$ ppts. NiCN, which can be redissolved in KCN to give the original material. (6)

D. $K_2Ni(CN)_3$ absorbs CO, supposedly giving $K_2[Ni(CN)_3CO]$ (12). It also absorbs C_2H_2 (12), and NO (13). Manchot believes that NO gives $K_2[Ni(CN)_3NO]$, but Job and Samuel say that the NO is reduced to NH_2OH and the Ni^{+1} is oxidized to Ni^{+3}

E. Reduction of Ni^{++} by a mixture of $NaNO_2$ and Na_2SO_2 gives two products, which are said to be $HN(SO_3H)(SO_3Ni).nH_2O$ and $Ni(OH)$. (15) These results seem doubtful.

F. Manchot and his coworkers have prepared many nitrosyl salts, which they claim contain univalent Fe, Co, and Ni. In an atmosphere of NO, cobalt salts react with $K_2S_2O_3$ to give $K_3\ Co(NO)_2(S_2O_3)_2$. The corresponding nickel salt is $K_3\ Ni(NO)(S_2O_3)_2$ (16). Mercaptans can be used instead of thiosulfates (17). The existence of univalent metal in these compounds has been denied by Cambi (18) and by Ormont (19).

IV. Trivalent Metals

A. Many cobalt ammines, cyanides and nitro compounds contain tripositive cobalt.

B. Cobaltic fluoride is readily obtained by the action of fluorine on cobalt salts; has been suggested as a fluorinating agent.

C. Oxidizing agents in alkaline media convert Co^{++} to $Co(OH)_3$. Even air will produce this change to some extent (21). In acid solution it is a powerful oxidizing agent.

D. Cobaltic sulfate can be prepared electrolytically and is a valuable oxidizing agent in organic reactions (22). Cobalt alum is well known (36).

E. Many attempts have been made to prepare $NiCl_3$ (23). Some of these gave red solns. which liberate 0.2-0.3 of an atom of "active" oxygen per nickel atom.

F. $Ni_2O_3.xH_2O$ is doubtful. Alkaline oxidizing agents give precipitates of varying composition, with ratios of Ni:O varying from 1:1.1 to 1:1.9. X-ray data show that these materials are NiO or mixtures of NiO and NiO_2 (24,25). Ott and Cairns, however, believe Ni_2O_3 to be a true compound (31). At lower temperature, NiO absorbs oxygen readily (26).
This material is the oxidizing agent in the Edison storage cell. While it is fairly stable when wet, it loses oxygen slowly in boiling water (27). Tanatar (28) believed it to be a peroxide but this is probably incorrect (29).

G. Schall and coworkers (23a,30) prepared $Ni(C_2H_3O_2)_3$ and $Co(C_2H_3O_2)_3$ by electrolysis of solutions of the diacetates in glacial acetic acid. The Ni^{+3} compound is deep green and the Co^{+3} compound apple green. They are decomposed by water. This work is rather doubtful, as the authors did not get consistent results.

H. Oxime compounds. Nickel formoxime in alkaline alcohol solutions absorb oxygen from the air to give a deep brown solution. A nickelic complex may be crystallized from the solution (32).

Benzamidoxime forms $\left(C_6H_5C\begin{matrix}NH_2\\NO\end{matrix}\right)_3 Ni$ (33).

V. Tetravalent metals.

A. Nickel dioxide almost certainly exists, although it has never been obtained pure. Preparations having as much as 1.9 atoms of oxygen per nickel atom can be prepared (34.35). It is a strong oxidizing agent, converting chlorides to chlorine, sulfites to dithionate, ammonia to nitrogen.

B. Cobalt dioxide has been reported from oxidation of Co^{++} in alkaline media (37).

C. If an alkaline solution containing Ni is heated with a strong oxidizing agent and dimethylglyoxime, no ppt. forms, but a deep red solution. From this solution, a compound of tetravalent nickel can be crystallized (38). It is said to be $(DH)_2NiO$.

C. (continued)
If a solution of it is acidified in the presence of KI, two equivalents of I_2 are liberated.

D. Polynuclear cobalt ammines. Werner prepared many polynuclear ammines containing peroxo bridges. Analysis indicated that some of these compounds contained both tervalent and tetravalent cobalt. (39) Examples are $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ and $(NH_3)_4Co\left(\begin{matrix}NH_2\\O_2\end{matrix}\right)Co(NH_3)_5]X_4$. Upon heating with H_2SO_4, such salts are decomposed to mononuclear ammines, with the liberation of gaseous oxygen. The ammount of oxygen liberated indicates one tetravalent cobalt atom. Titration with arsenite leads to the same conclusion (40).
The magnetic susceptibility of these compounds confirms the fact that the ion contains an unpaired electron (40,41) so the assumption of tetravalent cobalt is confirmed.

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THE BASICITY CHARACTERISTICS OF SCANDIUM, YTTRIUM, AND THE RARE EARTH ELEMENTS

Therald Moeller November 14, 1944

I. Introduction

While the term "basicity", as applied to the metallic elements in general, apparently covers all phenomena from the ease with which the free elements lose electrons to the extent to which oxygen containing salts of these elements are decomposed thermally, such phenomena are all manifestations of relative tendencies to lose or gain electrons and are thus reducible to acid-base characteristics in the G. N. Lewis sense.

Scandium, yttrium, and particularly the rare earth elements are generally recognized as yielding the most basic oxides of all the trivalent metals except actinium (11, 21, 69, 71, 73, 93, 99). As evidences of these relatively high basicities, one may cite the ease with which even the strongly ignited oxides dissolve in acids (69, 71, 73), react with ammonium salts both in solution and at elevated temperatures (43, 88), and absorb atmospheric carbon dioxide (69, 71, 73). Parallel evidences of high basicities are noted in the slight, though measurable, hydrolysis of aqueous salt solutions (10, 17, 18, 19, 57, 59, 60, 63, 70, 71, 73, 78, 92, 97) containing weakly basic anions, the comparatively high water solubilities and precipitation pH values of the hydrous oxides and hydroxides (16, 20, 21, 24, 63, 66, 74, 81, 90, 94, 96), the relatively high temperatures required for the decompositions of oxygen-containing salts (102, 103, 104), and the low ionization potentials of the free elements (89).

Significant basicity differences, especially between scandium and yttrium, yttrium and lanthanum, and lanthanum and lutecium, are apparent. Because of the excellent agreement between theoretically predicted basicity variations and those observed and because of the dependence of many separational procedures upon such basicity differences, a detailed examination of these phenomena is profitable.

II. Establishment of Relative Basicities

A. Theoretical Considerations.

Since the relative attractions for electrons are dependent upon atomic and ionic sizes (99), basicity predictions can be based upon size considerations. Atomic and molecular volumes for most of the elements and many of their compounds have been reported (6, 12, 13, 15, 44, 45, 46, 56, 62, 98). Data in Table I indicate the expected increases from scandium through yttrium to lanthanum. The decrease between lanthanum and lutecium (the lanthanide contraction) is ascribable to the increased nuclear charges and the simultaneous filling of the 4f orbitals. Paralleling atomic and molecular size variations are variations in the radii of the trivalent ions, the empirical and calculated values for which are listed. Basicity decreases should parallel size decreases. The combined effects of cation charge and size are given by the ionic potentials of Cartledge (25), and the relation between size and ionization potential is apparent.

Size and charge-size considerations would predict lower basicities for materials in a +4 oxidation state and higher basicities for those in a +2 state. The reported amphoterism of CeO_2 (26,93), Pr_6O_{11} (4), and Tb_4O_7(4) and the ease of hydrolysis of Ce(IV) salts (9,22,55,93) confirm the lowered basicities of high valent materials. Although amphoterism has been reported for La_2O_3 (3), this is doubtful (105).

B. Experimental Establishment of Relative Basicities

1. Order of Precipitation by Alkalies. From a mixture of rare earth salts in solution, soluble alkalies will precipitate the least basic materials first. Scandium has thus been shown to be the weakest base, and basicity decreases from lanthanum down through lutecium (11, 71, 73, 92, 93). Yttrium, however, appears to be as highly basic as the cenium earths, a position which may be ascribable to a concentration effect (96). Early work showed gadolinium to be more basic than samarium (5, 8, 30), but more careful procedures have reversed this order (47).

2. Precipitation and Dissolution of Hydrous Oxides and Hydroxides. Solubility studies (24, 39, 64) and electrometric measurements upon alkali titrations (16, 20, 21, 66, 74, 81, 90, 94) have indicated decreasing basicities in the series lanthanum to lutecium, with yttrium occupying a place close to holmium and scandium following lutecium. Comparisons of solubility product constants, assuming the precipitation of hydrous hydroxides (54, 101), have lead to an order of comparative basicities paralleling an order of comparative ionic radii (39, 74). (See Table I)

3. Hydrolysis Studies. The hydrolysis of rare earth salt solutions has been measured by determination of conductivities (10, 17, 18, 57, 70), by measurement of hydrogen ion concentration (10, 60, 78), by determination of free acid through extraction (97), and by the effects of the liberated hydrogen ion upon the hydrolysis of esters (17, 18, 70), the inversion of sucrose (18), and the reduction of iodate with iodide (59). In addition the evolution of carbon dioxide from hydrolyzed carbonates has been measured (19). Precipitation of basic salts, for example nitrites, has been investigated (53, 92).

4. Thermal Decompositions to Basic Salts or Oxides. Measurement of the decomposition temperatures of the anhydrous sulfates (102, 103, 104) has shown that decomposition temperature rises with increasing basicity of the element concerned. Such basicity series do not agree too well with those arrived at by other means.

5. Thermo-Chemical Investigations. The heat of reaction of the trivalent oxide with hydrochloric acid has been found to increase in the series samarium, neodymium, praseodymium, lanthanum (72).

6. Electrode Potentials. Although no direct relation exists between basicity and electrode potential, Heyrovsky (49) has derived an expression relating basicity, electrode potential, and cation mass. The only measurements approaching electrode potentials are the polarographic data of Noddack and Brukl (80), but although these authors point out a basicity relation, it appears that a portion of their data represents reduction of the hydrogen ion (50, 64) and application of their figures to the Heyrovsky relation is impractical. The approximate potentials listed by Latimer (68) indicate lanthanum to be the most basic and scandium the least.

C. Summary

Basicity summaries based upon a variety of results (1, 11, 19, 21, 39, 51, 59, 60, 61, 69, 71, 73, 74, 92, 99) indicate basicity to decrease in the order La, Ce(III), Pr, Nd, Il, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc, Ce(IV).

III. Separations Based upon Basicity Differences

Procedures of this type have been most successful in the removal of lanthanum, cerium, thorium, and scandium and in a preliminary fractionation of the yttrium sub-group. Although any precipitation method may, in a sense be regarded as a basicity method, only those directly involving the hydrogen or hydroxyl ions need be listed. Typical procedures are:

1. Precipitation by Alkaline Materials. The caustic alkalies (5, 8, 16, 30), ammonia (5, 8, 33, 42, 52, 82-87, 91, 95), magnesia (76, 91) rare earth oxides (100), organic bases (48, 58), oxides and carbonates (78), and urea (41, 91) have been employed. The controllable pH achieved in urea (41) and in ammonia systems containing complex-forming cations or ammonium salts (82-87) have proved useful.

2. Hydrolysis. Oxidation of cerium followed by hydrolysis is the common method for removing this element (22, 23, 69, 71, 73, 75). Fractional hydrolysis of such salts are the azides (1, 29, 32, 34) and the nitrites (14, 52, 53, 92) has yielded excellent results, especially in yttrium sub-group separations.

3. Hydrolysis by Means of Electrolysis. First employed by Krüss (67), electrolysis of mixed salt solutions, usually with mercury cathodes, has given excellent results (2, 33, 35-37, 65, 77, 91), the least basic materials separating first.

4. Fractional Solution of Oxides Acids. Although not widely applied, this procedure has been used with some success (26, 42, 75).

5. Fractional Thermal Decomposition of Oxygen-Containing Salts. Favored among such procedures is the nitrate fusion process of Berlin (7) which has been employed by many workers, especially in the separation of the yttrium earths (14, 27, 28, 31, 38, 40, 55, 79). Thermal decomposition of sulfates at controlled temperatures has not proved effective (102).

TABLE I

Summary of Properties

Symbol	At. No.	Mol. Vol — cc. R_2O_3 (45)	Mol. Vol — cc. $R_2(SO_4)_3 \cdot 8H_2O$ (98)	Rad. of R^{+++} — Å Emp. (44)	Rad. of R^{+++} — Å Calc. (46)	Ionic Pot. (25)	Atomic Vol. — cc. (13, 62)	Ioniz. Pot. — e.v. (89)	Pptn. pH (66)	Soly. of $R(OH)_3$ $\times 10^6$ (74)	Basicity of $R(OH)_3$ rel. to $Y(OH)_3$ (39)	Basicity of $R(OH)_3$ rel. to $Y(OH)_3$ (74)
La	57	50.28[x]	---	1.22	1.004	2.46	22.43	5.49	7.82	7.8	1300	1235
Ce	58	47.89[x]	---	1.18	0.939	2.54	20.70	----	7.60	4.8	---	185
Pr	59	46.65[x]	253.9	1.16	0.910	2.58	20.79	5.76	7.35	5.4	80	333
Nd	60	46.55[x]	252.4	1.15	0.900	2.61	20.62	6.31	7.00	2.7	47	23.5
Il	61	-----	-----	-----	-----	----	-----	----	----	---	---	---
Sm	62	48.39	247.9	1.13	0.872	2.65	21.70	6.55	6.92	2.0	---	8.4
Eu	63	48.28	247.3	1.13	0.871	2.65	29.00	----	6.82	1.4	---	4.2
Gd	64	47.58	246.4	1.11	0.861	2.70	19.79	6.65	6.83	1.4	3.4	2.6
Tb	65	46.38	-----	1.09	0.845	2.75	19.11	6.74	----	---	----	---
Dy	66	45.49	242.8	1.07	0.832	2.80	18.97	6.82	----	---	0.5	----
Y	39	45.13	240.8	1.06	0.827	2.83	20.46	----	6.95	1.2	1.0	1.0
Ho	67	44.89	241.1	1.05	0.823	2.86	18.65	----	----	---	---	---
Er	68	44.38	239.3	1.04	0.816	2.88	18.29	----	6.76	0.8	---	0.16
Tm	69	44.11	-----	1.04	0.812	2.88	18.12	----	6.40	0.6	---	0.041
Yb	70	42.5	235.1	1.00	0.789	3.00	24.76	7.06	6.30	0.5	---	0.036
Lu	71	42.25	234.[illegible]	0.99	0.785	3.03	17.96	----	6.30	0.5	---	0.031
Sc	21	35.55	-----	0.83	0.681	3.62	-----	----	6.10°	---	---	---

[x] A

° (94)

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THE OXIDATION-REDUCTION POTENTIALS OF VANADIUM

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I. Introduction.

Vanadium exists in aqueous solution in the oxidation states 2, 3, 4 and 5. Including the metal itself, there are five oxidation states to be considered, and therefore four oxidation-reduction couples for which electrode potentials can be given.

Theoretically, it would be advantageous to write two electrode reactions for each couple, corresponding to the behavior in acid and alkaline solution. Measurements have been made in acid solution for the couples 2,3; 3,4 and 4,5. In alkaline solution, no measurements have been made, and the solubilities of the hydroxides $V(OH)_2$, $V(OH)_3$ and $VO(OH)_2$ are not known. Moreover, the formation of polyvanadates makes the +5 oxidation state extremely complex in any but strongly acid solution. The discussion will, therefore, be limited to the measurement of the three couples noted above in acid solution, and to an estimation of the potential of the couple V, V^{++} from heat and entropy data.

II. The vanadium (IV) - vanadium (V) couple.

Several measurements of cells involving tetravalent and pentavalent vanadium have been made (1, 2, 3, 4). Foerst and Böttcher (2) give evidence for a half-cell reaction,

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{++} + H_2O \qquad (1)$$

but uncertain liquid junction potentials diminish the reliability of the measurements. Coryell and Yost (3) have eliminated the liquid junction potential by measuring the cell

$$Pt,\ VO_2^+(C_1) + VO^{++}(C_2) + HCl(C_3),\ HCl(C_3),\ Hg_2Cl_2,\ Hg \qquad (2)$$

but regard the pentavalent vanadium to exist predominantly as HVO_3, giving the electrode reaction

$$HVO_3 + 3H^+ + 2e^- \rightleftharpoons VO^{++} + 2H_2O$$

Solubility data (5) (3) of V_2O_5 in HNO_3, HCl and $HClO_4$ indicate that the pentavalent vanadium is present as VO_2^+ or its equivalent $V(OH)_4^+$. Carpenter (4) made measurements which confirmed the half-cell reaction (1) and recalculated the data of Coryell and Yost on the same basis.

The E.M.F. of cell (2) was extrapolated to zero concentration keeping $C_2/C_1.C_3$ constant. Correcting for the potential of the calomel electrode gave $E^\circ = -1.00$ volt.

III. The vanadium (III) - vanadium (IV) couple.

Rutter (1) measured the E.M.F. of the cell

$$Pt,\ VOSO_4 + V_2(SO_4)_3 + H_2SO_4(0.25\underline{M}),\ H_2SO_4(0.25\underline{M}),\ Hg_2SO_4,\ Hg$$

keeping the total vanadium concentration 1M, varying the ratio of V(III) to V(IV) over wide limits. Based upon these measurements, Abegg, A erbach and Luther (6) give $E^\circ = -0.4$ volt for the reaction

$$V^{+++} + H_2O \rightleftharpoons VO^{++} + 2H^+ + 2e^- \qquad (4)$$

whereas Gerke (7) computes

$$1/2(VO)_2SO_4 + 1/2SO_4^{=} \;=\!=\!=\!=\!=\; VOSO_4 + e^-,\ E^\circ = -0.30 \text{ volt} \quad (5)$$

Foerster and Böttcher (2) measured a similar cell with V(III) and V(IV) concentrations kept equal. The total V concentration and H_2SO_4 concentration were varied but the latter was not kept equal on the two sides of the cell. Hence, a liquid juction potential was included. Latimer (8) gives $E^\circ = -0.314$ volt with a reference to Foerster and Böttcher.

The best measurements are those of Jones and Colvin (9) who measured the E.M.F. of a series of cells

$$Pt,\ VOSO_4(C_4) + 1/2V_2(SO_4)_3(C_3) + H_2SO_4(C_1),\ H_2SO_4(C_1),\ Hg_2SO_4,\ Hg$$

1. keeping C_1 constant, varying C_4/C_3.

2. keeping $C_4/C_3 = 1$, varying C_1 from 1 to 0.02

The results were calculated by

1. extrapolating E.M.F. to zero vanadium concentration, at each acid concentration.

2. extrapolating to zero concentration of vanadium and acid (zero ionic strength) using the Debye-Hückel theory as a guide. The result is that $E^\circ = -0.337$ volt at 25°.

IV. The vanadium (II) - vanadium (III) couple.

The history of the investigation of the vanadous-vanadic couple parallels closely that of the vanadic-vanadyl couple. The earliest study was that of Rutter (13) who measured the EMF. of the cell

$$Pt,\ 1/2V_2(SO_4)_3 + VSO_4 + H_2SO_4(0.25\underline{M}),\ H_2SO_4(0.25\underline{M}),\ Hg_2SO_4, Hg$$

and found a value of $E^\circ = +0.210$ volt.

Foerster and Böttcher (2) also made some similar measurements. They found that variable potentials were obtained when using platinum electrodes owing to the evolution of hydrogen but that if mercury electrode is used, the difficulty is eliminated. This "mixed potential" behavior of electrodes has been described in other cases (10, 11). However, Foerster and Bottcher failed to remove the liquid junction potential.

Jones and Colvin (12) measured the E.M.F. of the cell

$$Hg,\ 1/2V_2(SO_4)_3(C_3) + VSO_4(C_2) + H_2SO_4(C_1),\ H_2SO_4(C_1),\ Hg_2SO_4,\ Hg.$$

and calculated the results in much the same way as explained above for the vanadic-vanadyl couple. They found that $E^\circ = +0.255$ volt at 25°.

V. The vanadium - vanadium (II) couple

The potential of this couple has never been measured, and the measurement in aqueous solution appears to be impossible. In acid solution, the metal would rapidly react with hydrogen, if its behavior were reversible. Actually, it does not give reversible electrode behavior either in acid or alkaline solution.

Latimer (8) estimates from the free energy of formation of vanadous oxide and the free energy of solution of the oxide in acid, a value of E° = Ca. 1.8 volts. From the heat of hydration of vanadous oxide and the solubility of vanadous hydroxide, a value of E° = Ca 1.2 volts is estimated. A final estimate of 1.5 $\pm$ 0.3 volt is given. No source of the data is indicated, except for the heat of formation data which were listed by Bichowsky and Rossini (14).

The following sample calculation will serve to illustrate the estimation of the electrode potential in cases where experimental data are scanty.

Given that the heat of formation of V_2O_2 is -195 kcal. (14,15) and estimating the entropy of V_2O_2 to be twice that of MnO (16) which is 14.4 cal./deg. mole, the free energy of formation of V_2O_2 is -185 kcal., compared with Latimer's(8) value of 182 kcal.

To estimate the free energy of the reaction

$$V_2O_2 + 4H^+ \longrightarrow 2V^{++} + 2H_2O \qquad (6)$$

we will first find the heat of reaction between MnO and HCl or HNO_3. The heats of formation of $MnCl_2$ (aq) (17), MnO (S) (18) and HCl (aq) (19) are respectively 128.7, 96.5 and 39.7 kcal./mole., giving a heat of reaction of -47.2 kcal. Using $Mn(NO_3)_2$(aq) (17) and HNO_3 (aq) (14), the heats of formation are 147.8 and 49.2 kcal. giving a heat of reaction of -47.1 kcal. for the reaction.

$$MnO + 2H^+ \longrightarrow Mn^{++} + H_2O$$

Apparently, no entropy data exist for Mn^{++}, but for the analagous reaction of FeO to give Fe^{++}, the entropy of H^+ is zero by convention, that of Fe^{++} is -25.9 (20), that of H_2O is 16.75 (21,22) and that of FeO is 14.2 cal./mole deg. (16). The entropy change is -23.4. Assuming for the V_2O_2 reaction an entropy change of twice this amount, the free energy change of reaction (6) becomes 80 kcal. Subtracting the free energy of formation of two moles of water we have

$$\begin{array}{lllll}
2V + O_2 & \longrightarrow & V_2O_2 & & \Delta F^\circ = -185 \\
V_2O_2 + 4H^+ & \longrightarrow & 2V^{++} & + 2H_2O & \Delta F^\circ = -80 \\
2H_2O & \longrightarrow & 2H_2 & + O_2 & \Delta F^\circ = 113 \\
\hline
2V + 4H^+ & \longrightarrow & 2V^{++} & + 2H_2 & \Delta F^\circ = -152 \text{ kcal.}
\end{array}$$

The standard potential is calculated from the equation

$$E^\circ = -\Delta F^\circ/nF = 152/4 \times 23.06 = 1.7 \text{ volts.}$$

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THE HONORABLE ROBERT BOYLE

Virginia Bartow November 28, 1944

I. Youth 1626-1644
   1. Born, Lismore, Ireland, a fourteenth child, January 25, 1626.
   2. Mother, Katherine Fenton, daughter of Sir Geeffrey Fenton, Secretary of State for Ireland.
   3. Father, Richard Boyle, the Great Earl of Cork, Lord Justice of Ireland -- Elizabethan, Protestant, Royalist -- "the richest man in Great Britain and the most influential in Ireland".
   4. Family, eleven brothers and sisters completely involved in the court, the society and political struggles of the period.
   5. Training
      a. Foster parents -- Irish peasants
      b. Eton -- tutor under Sir Henry Wottan, cousin of Francis Bacon
      c. Geneva -- tutor a strict Calvinist.
      d. Italian travels -- Florence at end of the life of Galelio.

II. Period of study and apprenticeship 1644-1660
   1. English Civil War, Parlimentary Rule
   2. Politics -- a cavalier -- sympathy with the Commonwealth.
   3. Abode -- Stallbridge Manor
      a. Gentleman farmer
      b. Experimentalist and Philosopher
      c. Alchemist
   4. London -- with Lady Ranelagh, Katherine Boyle, a Parlimentarian.
      a. The "Invisible College", Wallis, Willis, Wren, Barlow, Hooke, Evelyn.
      b. Milton
   5. Oxford, study of natural science -- the Purge -- Bodleian Library.
   6. Publications of importance
      "Occasional Reflections"
      "Seraphic Love"
      "Some Considerations concerning the Style of the Holy Bible"
      "The Martyrdom of Theodora and Didymus"

III. Period of Productivity 1660-1670
   1. Restoration
   2. The Plague and The Fire
   3. The Royal Society
   4. Publications
      1660 "The Spring of the Air"
      1661 "The Skeptical Chemist"
      Numerous Scientific Papers on Color, Cold, Corpuscular Theory, etc.

IV. Last Years 1670-1691
1. Abode -- London on Pall Mall -- ill health
2. Religious views -- leader of Anglican Church, the "via media" between Romanism and Protestantism
3. Positions offered and rejected.
a. Peerage by Charles II
b. High Place in the church upon taking holy orders.
c. Presidency of the Royal Society
d. Provost of Eton
4. Positions held
a. Governorship for the Society for the Propagation of the Gospel in New England
b. Membership on the Company of the Royal Mines
c. Director of the East India Company
d. Oxford, Doctor of Physic
5. Achievements
a. "Father of Chemistry"
1. An Historian
2. Founder of analytical chemistry
3. Clear enunciation of the idea of chemical elements
4. Proof air needed for combustion
b. Discoverer with Hooke of the Ideal Gas Law
c. Supersederof scholasticism of Aristotle and medieval philosophy of Paracelsus with Baconian induction or the "New Philosophy".
d. Purpose -- "To consecrate his scientific labors for a witness to God's creation and governance of the universe."
6. Death -- London, at Lady Ranelagh's December 30, 1691.
a. Boyle Lectureship
b. "Not sure science is good for world."

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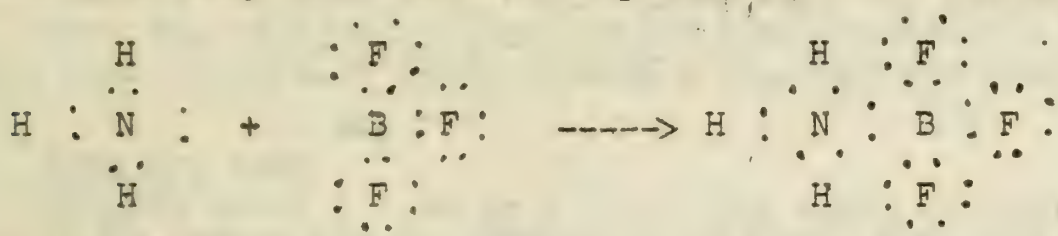
COORDINATION COMPOUNDS OF BORON TRIFLUORIDE

Donald Ray Martin December 5, 1944

Although boron trifluoride was discovered over one-hundred and thirty years ago (35), knowledge of the many coordination compounds, which it is capable of forming, is comparatively recent. On the basis of the electronic structure of boron trifluoride, the boron atom should be a good acceptor of electrons and boron trifluoride should form many coordination compounds by the following mechanism:



Actually the number of such compounds is astonishingly great while the number of different atoms, which have been found to donate to the boron atom, is surprisingly small.

These addition compounds will be discussed according to the groups in the Periodic Table of which the donor atom is a member.

Group 0. Argon has been found by Booth and Willson (15) to form six coordination compounds with BF_3 at low temperatures under pressure. See Table I.

Groups I, II, III. As would be expected from the fact that they are polar, none of the members of these groups have been reported as donors to the boron atom of BF_3.

Group IV. Although no coordination compounds have been isolated in which the donor atom is a member of Group IV, it has been postulated that the carbon atom, in olefin compounds, is the donor to the boron atom of BF_3 in condensation and polymerization reactions in which BF_3 is the catalyst (11) (33) (36) (52) (55) (56) (77).

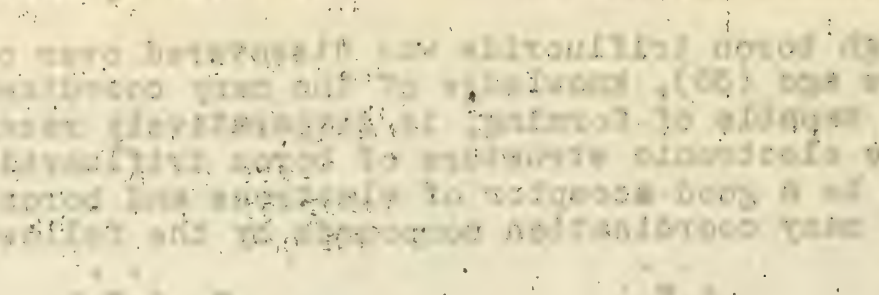
BF_3 has been reported to be unreactive toward CH_4, closed chain compounds, e.g. C_6H_6 and CO (33).

Krause and Knobbe (47) reported a reaction between a saturated hydrocarbon and BF_3 in which tertiary butyl boron fluoride was formed.

Group V. Nitrogen: The nitrogen atom in its compounds forms quite a few coordination compounds with BF_3. These may be of the type:

$N.BF_3$, where N is ammonia (1)(27)(34)(70), trimethyl amine (17)(23)(65), triethyl amine (46), diethyl amine (46), ethylamine (46), acetamide (16), aniline (50)(79)(84), dimethylaniline (17)(69)(84), acetanilide(84), methyl acetanilide(84), monosodium- and monopotassium-aniline (64), benzalaniline (81), p-aminobenzoic acid (83), acetophenone oxime (41), p-tolylphenyl ketoxime (41), pyridine (21)(87), quinoline (16), piperidine (16).

$2N.BF_3$, where N is ammonia (27)(34)(79)
$3N.BF_3$ where N is ammonia (27)(79)
$N.2BF_3$ where N is pyridine (16) and brucine (50)
$N.4BF_3$ where N is hexamethylenetetramine (91)
$RCN.BF_3$ where R is H, CH_3, C_6H_5, $H_3C-C_6H_4$ (76)
N_2O is unreactive with BF_3 at low temperatures (13).



Phosphorus. Only phosphine has been reported to donate to BF_3, forming the compounds $H_3P.BF_3$ (89) and $H_3P.2BF_3$ (10)(89).

Group VI. Oxygen-inorganic. Oxygen in inorganic compounds seems to be a better donor when it is not attached to another atom by a double bond. The types of compounds reported are:

$HOH.BF_3$ (63)(68)(86); $H_2O.BF_3.2C_{10}H_{18}O$ and $H_2O.BF_3.C_4H_8O_2$ (63)(68). $2HOH.BF_3$ (2)(3)(4)(9)(33)(35)(51)(60)(63)(68)(92); dihydroxyfluoboric acid $H_2O.BF_2.OH$ (48); $2H_2O.BF_3.2C_{10}H_{18}O$ and $2H_2O.BF_3.C_4H_8O_2$ (63)(68)

BF_3

$3HOH.BF_3$ (59)
$MOH.BF_3$ where M = Na or K (68), Ca, H_2PO_3 or $H_3P_2O_6$ (45)
$MO.BF_3$ where M = Ca (29), B_2O_2 (5)(80), P_2O_4 (37)(40)
$M_2O.4BF_3$ where M = alkali metal or NH_4 (85)
$M_2SO_4.BF_3$ where M = Na, K, Tl, ($Cs.2BF_3$) (6)(7)
$Na_3PO_4.3BF_3$, $K_3PO_4.3BF_3$, $Na_4P_2O_7.4BF_3$, $K_4P_2O_7.4BF_3$ (6)
$NaOCH_3.BF_3$, $KOCH_3.BF_3$ (68), $Hg(OCH_3.BF_3)_2$ (75)
$POF_3.BF_3$ (14); $POCl_3$, SO_2Cl_2 do not react (22)
See table III.

Oxygen-organic. As early as 1878 Landolph (56) reported that BF_3 combines "equivalent for equivalent" with aldehydes, ketones and carbonyls." Gasselin (33) in 1894 observed that the presence of oxygen in an organic molecule is a favorable condition for coordination with BF_3. As will be shown below, an oxygen attached by a double bond does not coordinate with BF_3 as easily as an oxygen atom attached to two other atoms by single bonds.

Alcohols. Two series of compounds have been reported as formed by BF_3 and alcohols. They are:

$ROH.BF_3$ where R = CH_3 (33)(75)(88), C_2H_5 (16)(33), i-C_4H_9 (29) glycol (33)(68), C_6H_5 (82).
$2ROH.BF_3$ where R = CH_3, C_2H_5, n-C_3H_7, sec-C_3H_7, n-C_4H_9 (63)(68) CH_2ClCH_2, CCl_3CH_2 (68), $C_6H_5CH_2$ (24)(68), C_6H_5 (33) (68)

Meerwein and Pannwitz (68) concluded that the stability of BF_3-alcohol complexes is decreased if a polar or easily polarisable group, e.g. CH_2Cl, CCl_3, or C_6H_5, is in the immediate proximity of the hydroxyl group. See Table IV.

Aldehydes. Very few coordination compounds of BF_3 with aldehydes have been reported.

$RCHO.BF_3$ where R = CH_3, $(CH_3)_3C$, Cl_3C (20)

Valenic and benzyl aldehydes have been reported to react equivalent for equivalent with BF_3 (52)(55)(56).

Ketones. Only acetone (33) and benzoyl acetone (69) have been reported to form one to one coordination compounds with BF_3. BF_3 has been reported to react with acetone (20)(33)(50)(56)(57), methyl nonyl ketone, camphor (52)(53)(56) and benzoyl acetone (73).

Acids. Analogous to the alcohol compounds, we find two series of acid compounds with BF_3, namely:

$RCOOH.BF_3$ where R = H (68), CH_3 (43)(62)(63)(68), C_2H_5 (16)(68) n-C_3H_7 (68), $H_2COH = CH$ (68), COOH (68), $COOH(CH)_2$ (68), $COOH(CH_2)_2$ (68), C_6H_5 (16)(68), $C_6H_5CH_2$ (68)

$2RCOOH.BF_3$ where R = H (68), CH_3 (16)(44)(63)(64)(68), CH_2Cl (16) (63)(68), C_2H_5 (68), n-C_3H_7 (68), i-C_3H_7 (69), $H_2COH = CH$ (68),

Meerwein and Pannwitz draw the same conclusion about the stability of acid-BF_3 compounds that they did about alcohol-BF_3 compounds. Groxall, Sowa, and Nieuwland conclude that there is a greater tendency for BF_3 to coordinate with the carboxy or carbalkoxy groups than with the phenolic group (25). See Table V.

Ethers. The ether compounds with BF_3 are fairly well known. Those that have been reported are one to one compounds with methyl (18)(19) (31)(33)(38)(57a), ethyl (31)(33)(57a)(74)(90), methyl ethyl (57a)(66) methyl i-propyl (33), methyl amyl (67), n-propyl (65), i-propyl (18) (74), i-propyl phenyl (74), amyl (74), i-amyl (74), dibenzyl (74), ethyl benzyl (74), ethyl phenyl (16)(67), methyl phenyl (16)(67) ethers. Attempts with diphenyl ether have failed (16)(67). See Table VI.

$BF_3.2(n\text{-}C_4H_7)_2O$ has been reported by Meerwein and Pannwitz (68). Other miscellaneous compounds of the ether type are $C_4H_8O.BF_3$ (18) and the betaines produced by the reaction of BF_3 complexes with ethylene oxide or epichlorohydrin (65).

Acid anhydrides. $BF_3.O(CH_3CO)_2$ was reported in the same month in 1931 by Bowlus and Nieuwland (16) and by Morgan and Taylor (71). Two years later Meerwein (63) refuted their work and said the compound was $[(CH_3CO)_2CHCO]_2O.BF_3$. Similarly, he reported propionic, n-butyric, and i-butyric anhydrides to form compounds of the type $(RCOCHRCO)_2O.BF_3$. Later with i-butyric anhydride he reported $[i\text{-}C_3H_7CO.C(CH_3)_2.CO]_2O.3BF_3$, and with chloracetic and phenylacetic anhydrides, molecular compounds (69). With succinic, benzoic, and phthalic anhydrides Bowlus and Nieuwland (16) obtained no reaction, however $BF_3.O(H_2CCO)_2$ has since been reported (67).

Esters. Esters have been found to form stable coordination compounds with BF_3. The Notre Dame workers, studying the mechanism of the alkylation of benzene using BF_3 as a catalyst, have postulated the formation of an intermediate complex of an ester with BF_3 (26) (61). As a result, many BF_3-ester compounds have been postulated, but comparatively few isolated. Those isolated and reported are:

$CH_3.OCOR.BF_3$ where R = H (71), CH_3 (16)(71), CH_2OH (72), C_6H_5(72).
$C_2H_5.OCOR.BF_3$ where R = H (16)(71), CH_3 (16)(71), C_2H_5 (16).
$C_3H_7OCOCH_3.BF_3$ (16)

The following compounds absorbed one mole of BF_3 to form viscous liquids or crystalline compounds but existance of molecular compounds was not established: ethyl chloroacetate, ethyl trichloroacetate, ethyl benzoate, diethyl oxalate, diethyl malonate, diglycol acetate, phenyl acetate (16) and p-tolyl acetate (41)

Sulfur-inorganic: Sulfur in compounds such as H_2O (37), SO_2 (13), SOF_2 (14), has been found to be a donor to the boron atom of BF_3 forming one to one molecular compounds. See Table III. However, in compounds such as $SOCl_2$ (22) and PSF_3 (14) the sulfur atom did not donate.

Group VII. Fluorine. Booth and Carter (12) suggest that BF_3 is associated at a pressure around 10 atmospheres, which could only come about by $BF_2F \longrightarrow BF_3$. Berzelius (8) passed BF_3 into water and produced fluoboric acid, which can be written $HF.BF_3$. Landolph reported "hydroboric fluoride" which can be written $BF_3.3HF$ (54). More recently $BF_3.2HF$ has been reported (42).

Compounds of the type $MF_2.BF_3$ and $MF_2.2BF_3$ where M = Fe or Co have been reported (58). $2CaF_2.BF_3$ has also been isolated (39). The alkali metal fluorides form compounds $MF.BF_3$ (28)

Other miscellaneous compounds are $NOF.BF_3$ and $CH_3CO^+BF_4^-$. The chlorofluorides of methane have limited miscibility in BF_3.

Chlorine. A du Pont patent (29) claims that organic coordination compounds with BF_3 are released from the BF_3 by the addition of a halide of Na, Zn, Al, Cu, Pb, Fe, or Sn. The inorganic halide coordinates with the BF_3 and thus releases the organic compound. NaCl was an example cited.

HCl and CH_3 do not react with BF_3 (13)(38).

Group VIII. No compounds with elements in this group as donors have been reported.

Summary. The elements which in their compounds are donors to the boron atom of BF_3 are in a small area of the non-metallic part of the Periodic Table, thus

C N O F
P S Cl A.

TABLE	COMPOUND	MELTING POINT °C	BOILING POINT °C	REFERENCE
I	$A.BF_3$	-128.6		15
	$A.2BF_3$	-127.3		
	$A.3BF_3$	-128.3		
	$A.6BF_3$	-128.3		
	$A.8BF_3$	-128.4		
	$A.16BF_3$	-129.0		
II	$NH_3.BF_3$	180		46
	$C_2H_5NH_2.BF_3$	89		46
	$(C_2H_5)_2NH.BF_3$	160		46
	$(C_2H_5)_3N.BF_3$	29.5	80_3	46
	$(C_6H_5)(CH_3CO)HN.BF_3$	133		84
	$(C_6H_5)(CH_3CO)CH_3N.BF_3$	114		84
	$C_6H_5CH{:}NC_6H_5.BF_3$	135-45		81
	$C_6H_5(CNOH)CH_3.BF_3$	107-13		41
	$C_5H_5N.BF_3$	45	300	2187
	$HCN.BF_3$	40		76
	$CH_3CN.BF_3$	87	101_{752}	16
III	<u>oxygen:</u>			
	$H_2O.BF_3$	5.4-6		63 68
	$2H_2O.BF_3$	4.6-5	$58.5-60_{1.2}$; $46_{4.6-5}$	63 68
	$C_4H_8O_2.H_2O.BF_3$	128-30 (decomp.)		68
	$C_4H_8O_2.2H_2O.BF_3$	142		63 68
	$2C_{10}H_{18}O.H_2O.BF_3$	71-3		68
	$2C_{10}H_{18}O.2H_2O.BF_3$	59.5-61		63 68
	<u>Sulfur</u>			
	$H_2S.BF_3$	-137.0		37
	$SO_2.BF_3$	- 96.0		13
	$SOF_2.BF_3$	-140.8		14
IV	$CH_3OH.BF_3$	-19.4		75
	$C_2H_5OH.BF_3$	-19		16
	$(CH_2OH)_2.BF_3$	40-4		63, 68
	Dialcoholates			
	$2CH_3OH.BF_3$		58.9_4	63, 68
	$2C_2H_5OH.BF_3$		60_4; $51-2_{15}$	63, 68
	$2C_3H_7OH.BF_3$		56_2	63, 68
	$2C_4H\ OH.BF_3$		$64.5-70_3$	63, 68
	$2CH_2ClCH_2OH.BF_3$		$59_{2-2.5}$	63, 68
	$2CCl_3CH_2OH.BF_3$	40-2		68
V	$HCOOH.BF_3$	-20-1		68
	$CH_3COOH.BF_3$	-23-4	59_{13}; 62_{11}	62,68,69
	$C_2H_5COOH.BF_3$	-28-9		68
	$n-C_3H_7COOH.BF_3$	-29-30		68
	$CH_3CH{:}CHCOOH.BF_3$	-35-6		68
	$C_6H_5COOH.BF_3$	+90-1.5(decomp) (98 crude)		16, 68
	$C_6H_5CH_2COOH.BF_3$	+56-9(decomp)		68

TABLE	COMPOUND	MELTING POINT °C	BOILING POINT °C	REFERENCE
V (cont.)	$2HCOOH.BF_3$		$43-4_{11}$	68
	$2CH_3COOH.BF_3$		$53-4_{10}$; 140_{748}; 142	16, 68
	$2C_2H_5COOH.BF_3$		$60-60.5_{12}$; $62-3_{17}$	16, 68
	$2n-C_3H_7COOH.BF_3$		64_{11}	68
	$2i-C_3H_7COOH.BF_3$		$68-70_{15}$	69
	$2CH_3CH:CHCOOH.BF_3$		$81-2_{12.5}$	68
	$(COOH)_2.BF_3$	57-8(decomp.)		68
	$(CHCOOH)_2.BF_3$	75-82		68
	$(CH_2COOH)_2.BF_3$	84-4(decomp.)		68
VI	$(CH_3)_2O.BF_3$	-10-4	126-8	18,31,38 57a
	$(C_2H_5)_2O.BF_3$	-50-2;-60.4	123-5.7	18, 57a
	$(i-C_3H_7)_2O.BF_3$	68		18
	$(CH_3)(C_2H_5)O.BF_3$	-98	127	57a
	$(CH_3)(C_5H_{11})O.BF_3$	-41	$54.8-5_{10}$	67
	$(CH_3)(C_6H_5)O.BF_3$	-12-3		67
VII	$C_2H_5O_2CCH.BF_3$		102_{748}	16
	$CH_3O_2CCH_3.BF_3$	60	110_{739}	16
	$CH_3O_2CCH_2OH.BF_3$		60_3	72
	$C_2H_5O_2CCH_3.BF_3$	26	119_{739}	16
	$C_3H_7O_2CCH_3.BF_3$		126_{743}	16
	$C_6H_5O_2CCH_3.BF_3$	40-55		72
	$p-CH_3.C_6H_4O_2CCH_3.BF_3$	146-50		41
	$C_2H_5O_2CC_2H_5.BF_3$	33	116_{747}	16

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ROLL CALL

December 12, 1944

Aluminum Phosphide

T. G. Klose

The literature reports five binary compounds of phosphorus and aluminum -- Al_3P_5, Al_3P_7, Al_5P_3, Al_3P and AlP. Since the analyses of some of these compounds are unrecorded or questionable, an attempt was made to find the correct composition of aluminum phosphide(s).

Various preparative methods are given, the most successful one being the process in which a mixture of finely divided aluminum and phosphorus is heated in an atmosphere of phosphorus vapor.

A complete analysis of the product is given. This analysis is designed to calculate phosphide phosphorus, free aluminum, total aluminum and phosphorus pentoxide.

X-ray diffraction studies of the phosphide preparations were made to determine the free aluminum concentrations in the various samples. The results were in agreement with chemical analysis. X-ray studies also indicated that the chief constituent was AlP and was identical for all preparations regardless of the amount of free aluminum present.

Aluminum phosphide is dark-gray to yellowish-gray in color. It doesn't decompose at temperatures as high as 1000°C. It is easily hydrolyzed by acids, bases, or water, one of the products of the reaction being phosphine.

Reference:
White, W. E. and Bushey, A. H., J.A.C.S 66, 1666 (1944)

- -

Preparation of Potassium Chloroplatinite

James V. Quagliano

Yellow, insoluble potassium chloroplatinate is prepared by the reaction of solutions of chloroplatinic acid and potassium chloride:

$$H_2PtCl_6.6H_2O + 2KCl \longrightarrow K_2PtCl_6 + 2KCl + 6H_2O$$

The K_2PtCl_6 is suspended in water and reduced with freshly prepared SO_2-water. The vessel is placed on a steam bath and during the reduction process the solution is stirred constantly with a mechanical stirrer. Tetravalent platinum is reduced to the divalent state according to the following equation:

$$PtCl_6^{=} + SO_2 + 2H_2O \longrightarrow PtCl_4^{=} + SO_4^{=} + 2Cl^- + 4H^+$$

The "temperature of a steam bath" is indefinite and to insure complete reduction it is necessary to state the temperature range (85-90°C) to which the solution must be heated.

Hole Data

October 12, 1944

Aluminum Phosphide

T. O. Klaus

The lithium reports five binary compounds of phosphorus and aluminum — Li_3P_4, $AlLi_3$, $AlLi_2$, $AlLi_2P_4$ and AlP. Since the analysis zone of these compounds are determined by qualitatively, no attempt was made to find the correct composition of aluminum phosphide.

Various preparative methods are given, the most successful combining process in which a mixture of finely divided aluminum and phosphorus is heated in an atmosphere of phosphorus vapor.

A complete analysis of the product is given. This analysis includes to aluminum phosphide percentage, free aluminum, total aluminum and phosphorus impurities.

X-ray diffraction studies of the compound preparations were made to determine the free aluminum percentages in the various samples. The results were in agreement with chemical analysis. X-ray studies also indicated that the acid decomposition was all and was therefore for all preparations regardless of the amount of free aluminum present.

Aluminum phosphide is hydrolyzed to phosphine-gas in water. It dissolves in concentrated hydrochloric acid and in 10000 in water. It is soluble in acids, hence, in water, one of the products of the reaction being phosphine.

References:

Stock, H. E. and Mathey, A. G. A.C.G. 40, 1000 (1944)

Preparation of Potassium Chlorophosphate

Adam T. Campbell

Yellow, insoluble potassium chlorophosphate is prepared by the reaction of solutions of chlorophosphoric acid and potassium chloride:

$$KCl(Cl_2PO_2) + KCl \longrightarrow K_2(Cl_2PO_4) + HCl + HCl$$

The $K_2(Cl_2PO_4)$ is washed in water and washed with friendly property SO_2-water. The vessel is placed in a steam bath and during the reaction process the solution is stirred constantly with a mechanical stirrer. Intermediate phosphine is reduced to the diphenyl state according to the following equation:

$$2(Cl_2PO_2)^- + Cl_2 + SO_2 \longrightarrow 2(Cl_2PO_4)^- + SO_4^{=} + 2Cl^- + 4H^+$$

The "isolation" of a steam bath is beneficial and to insure complete reaction it is necessary to state the temperature range (60-80°C) in which the solution must be heated.

Amphiprotic Substances

Elizabeth W. Peel

Basic substances are proton acceptors (electron donors); acidic substances are proton donors (electron acceptrs). The former are exemplified by ammonia and amines, the latter by acids. Acetamide (CH_3CONH_2) in water solution is essentially neutral, since it will neither accept a proton from H_3O^+ nor donate one to OH^-, which ions are the strongest acid and base possible in water solution. In other solvents, however, it has been shown to possess both acid and basic properties. For instance, in glacial acetic acid solution, acetamide can be titrated with perchloric acid, the potentiometric curve showing it to be a weak base in this case. Also, in liquid ammonia, it will react with sodamide to give a sodium derivative, donating a proton to the NH_2^- ion, thus acting as an acid.

The authors of this article have investigated further the behavior of acetamide in these solvents, determining the freezing point curves for the systems CH_3CONH_2-CH_3COOH (1), and CH_3CONH_2-NH_3(2). In each case, they found definite evidence for a 1:1 compound between the two components.

In case (1), the compound melts incongruently, decomposing just below its melting point (about 0°C), so the curve shows a break, no maximum, at slightly more than 50 mole percent acetic acid. The compound was isolated and analyzed acidimetrically; it corresponds to the following:

$$CH_3CONH_2 + HC_2H_3O_2 \rightleftharpoons (CH_3CONH_3)^+ (C_2H_3O_2)^-$$

and may be called acetylamonium acetate.

In case (2), the compound decomposes well below its melting point, the break in the curve coming at about 70 mole percent ammonia. The compound was not isolated, since it is so unstable. It would correspond to:

$$CH_3CONH_2 + NH_3 \rightleftharpoons (CH_3CONH)^-(NH_4)^+$$

and may be called ammonium aquo-ammono-acetate.

Acetamide has thus been shown to be definitely amphiprotic.

Reference:
Sisler, Davidson, Stoenner and Lyon, J. Am. Chem. Soc. 66, 1888 (1944)

Basic substances are proton donors (electron acceptors) while substances are proton donors (electron acceptors). The former are amphiphilic by nature and active, the latter by nature. Acetyrile (CH_3COCH_3) in water solution is basically neutral, since it will neither accept a proton from H_2O nor donate one to OH^-. Acid sites are the strongest acid and have powerful in water solution. In other words, however, it has been seen to increase both acid and basic properties. For instance, in glacial acetic acid solution, acetonitrile can be titrated with perchloric acid, the protonation curve shows it to be a weak base in this down. Also, in liquid ammonia, it will react with ammonia to give a sodium derivative, donating a proton to the NH_4^+ ion, thus acting as an acid.

The authors of this article have investigated further the behavior of acetonitrile in these solvents, determining the freezing point curves for the systems CH_3COCH_3-CH_3COOH [1], and CH_3COCH_3-NH_3 [2]. In each case, they found certain eutectic mixtures for a 1:1 compound between the components.

In case [1], the compound melts incongruently, decomposing back below the melting point (about 8°C), as the curve shows a trend, or maximum, at slightly more than 50 mole percent acetic acid. The compound was isolated and analyzed analytically; it corresponds to the formula:

$$CH_3COCH_3 \cdot CH_3COOH \quad \text{or} \quad (CH_3COCH_3)^+ (CH_3CO_2)^-$$

and may be called acetylacetonium acetate.

In case (2), the compound decomposes well below its melting point, the curve rising at about 70 mole percent ammonia. The structure was not identified, since it is so unstable. It would correspond to:

$$CH_3COCH_3 \cdot NH_3, \text{ or } (CH_3COCH_2^-)(NH_4^+)$$

and may be called ammonium acetylacetonate.

Literature has been found to be partially explicitly.

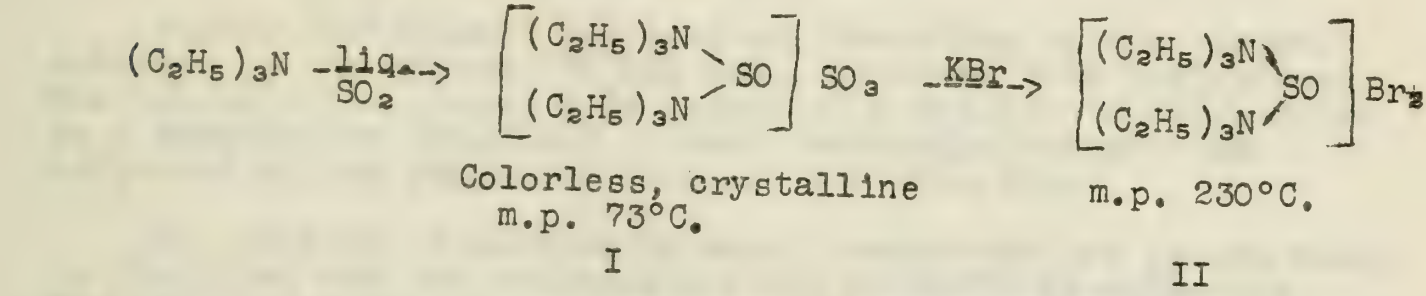
References:
Walter, Dreiden, Strasser und Lynn, J. Am. Chem. Soc. 66, 1948 (1944

Molecular Compounds Between Amines and Sulfur Dioxide. Comments on Jander's Theory of Ionic Reactions in Liquid Sulfur Dioxide.

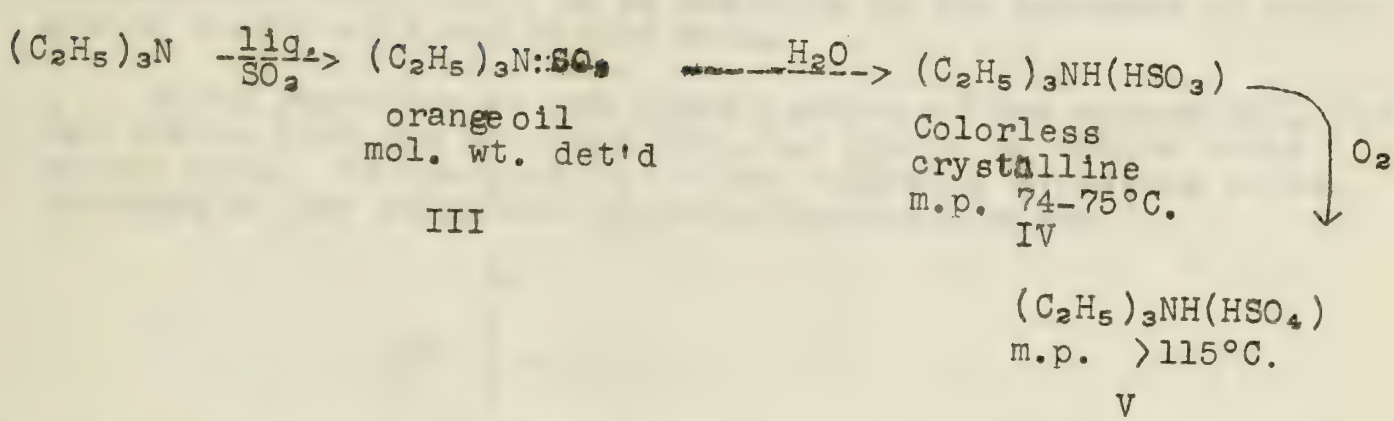
A. L. Oppegard

The authors claim that Jander's theory is based on experimental work which is not reliable. Errors were made in analyses, and molecular weight determinations were not made. The authors repeated Jander's work, but with vastly different results.

Jander's work and interpretation.



This article



It is pointed out that I and IV are probably the same compound and also that II was probably $(C_2H_5)_3N.HBr$ (m.p. 248°C) plus some IV.

Previous work on the reactions between amines and liquid sulfur dioxide indicates that they combine in a 1-1 ratio to give a simple molecular compound R_3N ----> SO_2.

On the basis of their work the authors conclude that reactions between amines and liquid sulfur dioxide are merely addition reactions and not ionic, as Jander states.

The exact structure of III puzzled the writers. The structure shown does not explain the intense color, nor the slight conductivity exhibited in liquid sulfur dioxide.

Reference.

L. C. Bateman, E. D. Hughes, C. K. Ingold, J. Chem. Soc. 243 (1944)

For a review of Jander's theory see Emeleus and Anderson, Modern Aspects of Inorganic Chemistry, page 482.

Polarizer Concentrix Between Active and Inactive Phases. Comments on Jackson's Theory of Chemi Ionization in Liquid Noble Gases.

The authors claim that Jackson's theory is based on experimental data which is not reliable. Errors were made in analyzing the polarizer output. Inaccuracies were not made. The authors repeat Jackson's work, but with nearly different results.

Jackson's work and interpretation.

$$(C_6H_6)_2 \xrightarrow{h\nu_0} \begin{bmatrix} [C_6H_6]_2^* \\ [C_6H_6]_2^{+} \end{bmatrix} \xrightarrow{80\%} \begin{bmatrix} [C_6H_6]_2^* \\ [C_6H_6]_2^{+} \end{bmatrix} \xrightarrow{20\%} \begin{bmatrix} [C_6H_6]_2^* \\ [C_6H_6]_2^{+} \end{bmatrix}$$

Solvation, Dissociation

C_6H_6, $TM^{+}_{C_6}$ C_6H_6, TCT^{+}_{C}

I II

This studies

$$[C_6H_6]_2^{+} \xrightarrow{h\nu_0} (C_6H_6)_2^{+}\text{Cons}_{\text{Ionization}} \longrightarrow (C_6H_6)_2^{+}\text{Ion}_{\text{Dissociative Ionization}}$$

$\text{Ion}_{\text{Ionization}}$, $\text{Ion}_{\text{Ionization}}$, $\text{Ion}_{\text{Ionization}}$

III IV

$(C_6H_6)_2\text{Ion}(\text{Ion}_{\text{Ionization}})$

V

It is pointed out that I and II are in-phase the same conditions and also that it was possible $[C_6H_6]_2$, C_6H_6, C_6H_6 plus some I.

Jackson's work on the equations between solids and liquid noble gases indicate that they combine in a 1-1 ratio to give a simple molecular complex. M^{+} ——— M^{*}.

On the basis of their work the authors consider that measurements between solids and liquid noble gases are merely elastic results and not hold as Jackson claims.

The main structure of III guided the writers. The elastic scattering does not explain the intense color, nor the slight conductivity exhibited in liquid noble gases.

References.

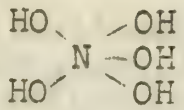
1. J. Jackson, D. J. Mayer, O. E. Jobin, J. Chem. Phys. XXI (1944)

For a review of Jackson's theory see Chemical and Activity, Volume Volume of Journal Chemistry, 1944.

The Structure of Orthonitric Acid

Hans B. Jonassen

When dry air is passed through a solution of dilute nitric acid at -15°C. needle-like crystals are obtained which have a composition corresponding to $HNO_3.2H_2O$. Erdmann (1)(2) and Mellor (3) assigned the following structure to this "compound":

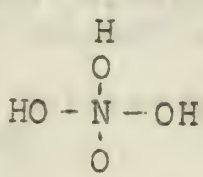


This compound is unstable above -15°C.

Küster and Kraumann (4) however, reporting on the thermal analysis of the system H_2O and HNO_3, obtained data indicating that no definite compound is formed at a position corresponding to a composition $HNO_3.2H_2O$. Their data only indicate the existence of the compounds $HNO_3.H_2O$ and $HNO_3.3H_2O$.

If, however, a mixture of acetic anhydride and nitric acid is distilled and the fraction boiling at 127°C is collected, analysis shows that the composition of this fraction corresponds to a compound $(CH_3COOH)_2.HNO_3$. This compound is called "Diacetyl Orthonitric" acid (2). It is unstable in the presence of water, giving acetic acid and nitric acid.

Biltz, reporting on his investigation of the system HNO_3 and H_2O, states that the compound $HNO_3.H_2O$ should be called ortho nitric acid. He assigned to it the following structure corresponding to the structure of orthophosphoric acid:

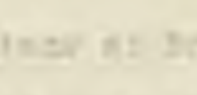


Zintl and Haucke (6) report in 1935 that they were able to isolate Na_3NO_4 and that they subjected this compound to x-ray investigations. These investigations seem to prove that during the formation of this compound from Na_2O and $NaNO_3$ the oxygen atom of the Na_2O is able to push aside the third oxygen atom of the nitrate ion to form the NO_4^{-3} ion which then acts as the central group of the compound. This compound is stable although the coordination number of nitrogen derived from the ratio of radius of cation/radius of anion gives a coordination number of three for nitrogen.

Zintl, Morawitz, and Waltersdorf (7) investigated also the orthonitric acid proposed by Biltz (5) by means of x-ray at -150°C. and at -80°C. They state that their data seem to indicate the same structure proposed by Biltz (5) for the orthonitric acid, because the x-ray pattern of this compound was somewhat

The Structure of Orthosilicic Acid Table 3, Diagram

When dry air is passed through a solution of silicic acid at -14°C, needle-like crystals are obtained which have a composition corresponding to $SiO_2.2H_2O$. Lehmann [1][2] and Meller (3) assigned the following structure to this "compound":

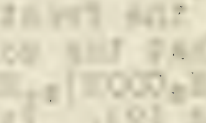


This compound is unstable above -14°C.

Meller ... Graham [1] however, according on the usual analysis of, in which H_2O and SiO_2, obtained data indicating that an orthosilicic acid is formed of a possible corresponding to a composition H_4SiO_4. Their data only indicate the existence of the compounds $SiO_2.2H_2O$ and $SiO_2.3H_2O$.

If, however, a mixture of equimolecular amounts and nitric acid is distilled and the fraction boiling at 187°C is collected, analysis shows that the composition of this fraction corresponds to a compound $(CH_3COO)_4.SiO_2$. This compound is called "tetraacetoxy orthosilicic acid [9]. It is soluble in the presence of water, giving silicic acid and acetic acid.

Data, regarding on the investigation of the system SiO_2 and H_2O, shows that the compound $SiO_2.4H_2O$ should be called ortho silicic acid. It assigned to it the following structure corresponding to the structure of orthosilicic acid:

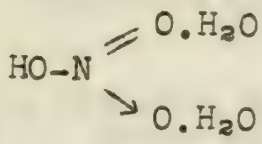


Last, and Morris [3] report to find that they were able to isolate H_4SiO_4, and that they substituted this compound to every investigation. Their investigations seem to prove that during the formation of silicic acid from SiO_2 and H_2O, the oxygen atom of the H_2O is used to pass, with the total oxygen atom of the silicic ion to form the SiO_4^{--} ion which then acts as the central atom of the compound. This conclusion is strongly argument the examination theory of Allright derived from the partial hydrolysis of certain derivatives of silicic acid which give a quadrivalent silicon for silicon.

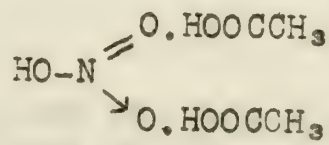
Just , Diamond, and Williamson [5] investigated also the polymeric acid formed by silica [6] by means of a study of -10°C and at -20°C. They state that their data seem to indicate the same structure assigned to silica [3] for the orthosilicic acid, namely the ring pattern of silicon tetrahedral was assumed

similar to that of the Na_3NO_4. They state, however, that the similarity is not outspoken enough to definitely prove this structure.

The "orthonitric" acid $HNO_3.2H_2O$ isolated by Erdmann (1)(2) and the related $HNO_3.2CH_3COOH$ seem only to be dipolar association compounds of the following structure:



and



This dipolar association seems to be substantiated by the following facts:

(1) "Diacetyl orthonitric" acid is unstable in the presence of water, forming acetic acid and nitric acid.

(2) This instability can be explained if dipolar association is assumed because in the case of such a linkage a group with a higher dipole moment may be assumed to displace one which has a lower dipole moment. The dipole moment of H_2O is 1.80 Debye units whereas that of CH_3COOH is 1.72 Debye units.

(3) Küster and Krumann were unable to show the presence of a compound corresponding to the composition $HNO_3.2H_2O$ in their thermal analysis data.

(4) Constant boiling nitric acid has the composition $HNO_3.2H_2O$.

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2. Erdmann, Z. angew. Chem. 16, 1079 (1903).

3. Mellor, Comprehensive Treatise of Inorg. Chem., Vol. VIII, p. 564.

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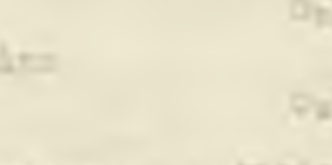
5. Biltz, W. Nachr. Ges. Wiss. Gottingen. Math. Phys. Kl. (N. F.) 1, 95 (1935).

6. Zintl and Haucke, Z. phys. Chem. A174, 314, (1935).

7. Zintl , Morawitz, and Waltersdorf, Naturw. 23, 197 (1935).

similar to that of the $BeSiO_4$. Other atoms, however, that the similarity is not outstanding enough to definitely prove this structure.

The "orthosilicate" with $SnO_2.SiO_2$ isolated by Tedesco (1)(4) and the related $MO_2.SiO_2.OOH$ were only to be similar associations analogous of the following structure:



This cloudy amorphous seems to be substantiated by the following facts:

(1) "Purity of orthosilicate" cited is unknown in the presence of water, forming metals acid and silicic acid.

(2) This instability was by confirmed if similar associations in Tedesco's Series in the case of such a tetrahedra a compound with a higher silicic content may be expected to isolate one which has a lower silicic content. The silicic content of MgO is 4.00 Cmgm with melting point of Cr_2O_3 is 1.99 Cmgm silica.

(3) Slater and Stresman were unable to show the presence of a reported orthosilicate in the composition $SnO_2.SiO_2$ in their thermal analysis data.

(4) Constant boiling nitric acid fed the compounds $SnO_2.SiO_2$.

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REACTIONS BETWEEN SOLIDS

Nancy Downs December 19, 1944

Introduction.

Reactions between solids have been employed for many years in industry but the study of such reactions is of comparatively recent origin. Since the beginning of these studies, over five hundred scientists have investigated solid reactions, approximately thirty-five of whom have been English or American (1)(2). Most of the work has been done on the interaction of metals with each other or the interaction of metallic oxides with other oxides or salts such as halides, sulfates, and silicates. Some studies of double decomposition reactions have been made.

History.

First work was done by Spring (1)(2)(3), and Sir Roberts-Austin about 1895 (2). Later Masing studied the effect of pressure on metal filings in bringing about a reaction. Cobb began the research of non-metallic compounds about 1910 (2). He suggested that a "quasivaporous" theory could be used to explain solid reactions (2). Taradoire claimed that for two solids to react, one had to have a vapor pressure. Also it was believed that the reaction didn't take place in the solid state but in a fused state or a gaseous state (4). Our modern conception of solid reactions has been built largely by the work of Tammann, Jander, Jost, Huttig, Hedvall, Hume and Calvin, Fischbeck, Seith, and Tubandt, in Europe (3)(2) and Ward and Wood in the United States.

Mechanism of Solid Reactions.

A. Four Stages in a solid reaction (5)(6).

1. A reaction takes place at the point of contact. It results in an increase of catalytic action.
2. The second step is the formation of a thin reacting layer or reaction skin. With the formation of this skin, there is a decrease in catalytic action, an increase in ability to absorb dyes and an increase in solubility in weak reagents (7)(8)(5)(9)(11).
3. The third step is the change of reaction layer and the formation of defective crystals.
4. The last step is the transformation of the defective crystals into pure crystals.

The four stages take place at two different rates. At first the reaction goes very rapidly, then it slows tends to slow down (10). The explanation of the rapid reaction rests on the fact that in the preparation of the mixtures by grinding or because of impurities present in the crystal, some crystals are deformed. The molecules, atoms, or ions which are moved out of place can change positions more easily at a lower temperature than perfect crystals will and the reaction occurs rapidly until the deformations are removed by the reaction or by recrystallization. Then the reaction slows down. The rates of the reactions depend upon the rate of diffusion and the rate of crystallographic changes (1)(2)(3)(11)(12).

REACTIONS BETWEEN SOLIDS

Henry Dunn September 13, 1944

Introduction.

Reactions between solids have been analyzed for many years in industry, in the study of such materials as cement, ceramics, and metals. Since the beginning of this century, physicists have established certain laws which govern the rate of reaction between solids. Most of the work has been done in the metallic field, where the reactions are important in the production of alloys or in the heat treatment of metals. Some studies of solids have been made in the electrical industry, and in addition, some work has been done in the study of the electrochemical reactions which have been made.

History.

About 1927 work was done by Spitzer (1)(2)(3), and Dr. Hedvig-Sandstedt (4). Later Wagner (5) made a direct attempt to relate rates of reaction to physical properties in a number of non-metallic compounds. Other researches, namely "Gasreaktionen" Essig (6) and Jander (7), investigated the thermodynamics of the solid state by using reactions involving vapor pressures. Also, it was believed that the reaction rate depended on the solid state but is a function of a phase change in the work of Tammann, Jander, Jander, Hedvall, Hedvall, and Tubandt. Recently (8)(9) work has been done in the United States.

Mechanism of Solid Reactions.

A. Four stages in a solid reaction (10).

1. A reaction takes place at the point of contact. It results in an increase of physical action.
2. The second step is the formation of a thin reacting layer by physical mass. With the formation of this solid, there is a decrease in concentration of solid reactants to equality to cause the reaction.
3. The third step is the diffusion of ions and in addition to equality to cause the reaction. In addition to equality to work through (11)(6)(7)(11).
4. The last step is the formation of reaction layer and the formation of reaction products.

The four stages take place at different rates. At first the reaction goes very rapidly, then it slows down to slow down (10). The mechanism of the solid reaction rests on the fact that in the preparation of the solid mixtures by grinding or powder of impurities present in the crystal, some crystals are deformed. The molecules, or ions which are moved out of place are those positions more easily so a later transformation than perfect crystals will and the reaction rates depends upon the activation are reduced by the reaction or by recrystallization. When the reaction slows down. The rate of the reaction depend upon the rate of diffusion and the rate of recrystallization (1)(2)(11).

B. Diffusion in solids (1)(3)(13).

1. Diffusion may occur in solids in one of three ways (13).
   a. Particles may pass along internal surfaces.
   b. Particles may pass in interstitially within the normal lattice.
   c. They may pass as a result of the vacant places within the lattice and movement of adjacent particles into the vacant positions (12)(6).
2. Tammann's equation (14)(15).

   Derived from Fick's law which may be stated mathematically:

$$dn = -QK \frac{dy}{dx}$$

   By substitutions and integration the following expression is obtained.

$$n = b \log t + c$$

   where n = quantity of substance which diffuses in terric t
   b = fraction of "diffusion threads" broken during given time.
   t = time
   c = constant

   If the percentage decomposition is plated against log t., a straight line is obtained. This seems to indicate a direct relationship between percentage decomposition and the rate of diffusion. Applications to actual data seem to prove the validity.
3. Jander's equation (14).

   This equation relates the thickness of the layer to the percentage decomposition.

$$\left(1 - \sqrt[3]{\frac{100-x}{100}}\right)^2 = \frac{2DCot}{r^2}$$

   x = the percentage decomposition.
   2DCot = the square of the thickness of the reaction layer.

   If the $\left(100 - \sqrt[3]{\frac{100-x}{100}}\right)^2$ is plotted against t a straight line is obtained.
4. Hume, Calvin, Topley equation.

   This equation is based on their belief that a crystallographic change takes place in a solid (14)(16). The rate at which the crystallographic change takes place is dependent on (a) the rate of nucleation, (b) rate of propagation of interfaces between the solids. In turn, the rate of solid reactions depends on rate of crystallographic changes in addition to diffusion.

   The equation relates the fraction decomposed to the time. (14)

$$= (Kt)^3 - 3(Kt)^2 + 3Kt$$

   These equations were applied to experiments by Wood and his coworkers and were found to agree quite well with experimental results.

C. Temperature affects the rate of reaction since it affects both the rate of diffusion and the rate of crystallization.

<u>Classification of solid reactions</u> (1)

A. Two elements

M' + M''

B. Two binary compounds with a common component.
$M'X' + M''X'$ or $M'X' + M'X''$
An example is the reaction of CaO with SiO_2.

C. Two binary compounds without a common component.
$M'X' + M''X''$

The first two types have been investigated to the greatest degree and the latter type perhaps has been neglected because no accurate quantitative methods were known.

Double decomposition reactions in the solid state.

Early work was done by Plato and Ruff (19) and Berketoff (17). More recently Tammann (15), Hedrall (3), Mathieu, Mathieu, and Paic(19), have done research on such equations.

Roland Ward and coworkers (14)(18) studied reactions between alumina and barium sulfate, and between ferric oxide and barium carbonate. From the results they obtained and from information they obtained by comparing their results to the Jander, Tammann, and Hume-Calvin-Topley equations, they set forth the idea that perhaps it is possible for the rate of crystallographic transition to be the deciding factor in the rate of certain chemical reactions.

L. J. Wood and his coworkers (17)(20)(21)(22)(23)(24) did a series of experiments on the reactions of solid alkali halides both above and below the fusion point, using an x-ray spectrograph to record the results. The results may be summarized as follows:

A. At temperatures above the fusion point (17)(20)(21).
1. In fifty seven out of the sixty reactions, the reactions went in such a way that the average cube edge of the stable pair was less than that of the reciprocal pair.
2. In fifty-seven of the sixty reactions, the sum of the heats of formation of the stable pair is greater than the sum of the heats of formation of the reciprocal pair.
3. The cation of the larger atomic weight unites with the anion of the larger atomic weight and the cation of the smaller atomic weight unites with the anion of the smaller atomic weight.
4. With the exception of the lithium salts, one member of the stable pair has the highest melting point of any of the four compounds formed.
5. In fifty-seven of the sixty reactions the reaction goes to completion as evidenced by
   a. Absence of x-ray patterns for two of the compounds involved.
   b. The cube edge of a resulting solid solutions is the same as the theoretical cube edge.

B. At temperatures below the fusion point (22)(23)
1. In the twelve reaction mixtures containing lithium salts and fluorides, the stable pair always had as a member, lithium fluoride. The stable pair in six cases contained the highest melting compound and in six cases the reciprocal pair contained the highest melting point.
2. If no fluorides are present in the lithium salts, the highest melting compound was found in every case in the reciprocal pair.

8. Two binary operations with a common component,
$$[x'] * [x'] \text{ or } [x'] + [x']$$
An example is the operation of set with [0].

9. The binary operations without a common component,
$$[x'] * [y'] \quad [x'] + [y']$$

The first two "pure" forms have been investigated in the previous chapter and the latter five primary has been neglected because of its quantitative output form above.

<u>Double discontinuity predicting in the entire state.</u>

Early work with those in Table 20, Table (19) and Table (17) Note especially Hansen (22) (Table) (3), Schiller, Barrows, and Zeigler have done research on such questions.

Schiel and Schwartz (19)(20) studied predictions between algebra and Boolean algebra, and between fuzzy sets and Boolean subsets. From the results they obtained and from information obtained by correlation theory in the future, Hansen, and Hansen Zeigler equations, that are lower, the idea that provides it is possible for the part of artificial intelligence intuition to be the Boolean factor in the form of fuzzy-logic structure.

1. 2. Wood and the Hansen (27)(28)(29)(30)(31) all a series of experiments on the operation of with atomic factors with those and below the fuzzy value, using an a-by experiment, [illegible] the results may be summarized as follows:

A. At temperatures above the Curie point (17)(20)(27)

1. In fuzzy across out of the fuzzy variables, the operation [illegible] it will, a may that the average value of the [illegible] fuzzy, the line [illegible] of the analytical [illegible]

2. Infinity-zero of the fuzzy predicting, the sum of [illegible] [illegible] of the atomic pair is greater than [illegible] the sum of the [illegible] of formation of the [illegible] pair.

3. The ratio of the [illegible] atomic weight within the [illegible] of the [illegible] atomic weight and the [illegible] of the [illegible] [illegible] with the ratio of the [illegible] [illegible].

4. With the exception of the [illegible] axis, the [illegible] of the atomic pair and the [illegible] melting point of [illegible] the four component form.

5. In fifty-zero of the fuzzy predicting the reaction [illegible] to [illegible] as evidenced by

a. Attempt of a-by [illegible] for the of the [illegible] involved.

b. The [illegible] of a predicting [illegible] [illegible] the data as the [illegible] [illegible].

B. At temperatures below the Curie point (20)(27)

1. In the fuzzy reaction analysis correlating [illegible] and the [illegible], the atomic pair always and as a [illegible] [illegible] fuzzy. The atomic pair in the [illegible] the highest melting [illegible] and in the [illegible] [illegible] pair contained the highest melting point.

2. If the fuzzy are present in the [illegible] [illegible] the highest melting [illegible] was found in every case in the [illegible] pair.

3. In the reactions involving no lithium salts, but fluorides, the highest melting component was contained in the stable pair.
4. For fifty-four of the sixty reactions, there was a complete or partial conversion of the reciprocal pair to the stable pair.
5. Little reaction occurs if the temperature is more than 200° below the fusion point and the reaction proceeds quite rapidly if the temperature is within 100° of the fusion point.

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INORGANIC CATALYSIS; INDUCED REACTION, PRECIPITATION, AND SOLUTION

F. W. Cagle, Jr. January 2, 1945

While the action of a catalyst either accelerates or diminishes the rate at which a reaction proceeds, it must be firmly understood that the presence of this catalyst in no fashion effects the extent to which the reaction will take place. The equilibrium conditions are uniquely determined for every reaction by the concentrations of the reactants and a choice of sufficient physical conditions. The calculation of this position of equilibrium is in the province of thermodynamics and if proper thermodynamic data are given, it can be calculated for any reaction for which the reactants and final products are known. This may be done without consideration of the intermediate products of the reaction.

In the field of rates of reaction, in which the art of catalysis finds its place, one discovers no "broad highway" which leads to success. In fact, one cannot set down a single general law or principle of catalysis. It is for this reason that the writer refers to catalysis (and related phenomena) as an art rather than a science. Knowing these things, we shall discuss catalysis only so far as the science is known and not attempt to draw general conclusions nor expect to see general principles resulting from this discussion.

The writer further desires to introduce with catalysis the induced reaction in which the "catalyst" suffers change in the reaction, for it seems that the exclusion of this kindred phenomenon would be not only highly arbitrary but objectionable as well. For the same reason, the phenomenon of induced precipitation and solution will be discussed.

It is of course evident that if a reaction could be found which is catalyzed by a certain element or radical in a mixture but not catalyzed by other substances, one could detect very small amounts of the catalyst by observing its effect upon the reaction.

1. Catalysis Due to Complex Formation

   a. The reduction of Ce^{+4} salts by dilute HCl proceeds very slowly at room temperature. This may be much accelerated by the formation of $HgAgCl_2$ (1,2).

   b. Chlorates in a neutral or mildly acid solution are only very weak oxidizing agents. The addition of a trace of OsO_4 suffices to make them behave as powerful oxidizing agents. It can be shown that the solubility of $KClO_3$ is markedly greater in neutral OsO_4 solutions than in water. Further the oxidation potential of such a solution is much greater than that of a solution of $KClO_3$ alone. This has been interpreted as indicative of the formation of a complex $KClO_3$-OsO_4 (3, 4, 5).

2. Catalysis Due to Principal Valence Compounds Compounds

THEORAVIT CATALYSTS: ESTUDIO RELATIVO, RECIPITATION, LOS DIVINOS

F. V. Cagle, Jr. January 5, 1949

While the action of a catalyst either accelerates or diminishes the rate at which a reaction proceeds, it must be firmly understood that the presence of this catalyst in no fashion alters the extent to which the reaction will take place. The conditions which are uniquely determined for every reaction by the concentrations of the reactants and a choice of particularly physical constants. The calculation of this position of equilibrium is in the province of thermodynamics and if proper thermodynamic data are given, it can be calculated for any reaction for which the reactants and final products are known. This may be done without consideration of the intermediate products of the reaction.

In the field of rules of reaction, in which the art of catalysis finds its place, one discovers no "broad highway" which leads to success. In fact, one cannot set down a single general law or principle of catalysis. It is for this reason that the writer refers to catalysis (and related phenomena) as an art rather than a science. Dealing these things, we shall discuss catalysis only so far as the science is known and not attempt to give general generalizations nor experts to see general principles resulting from this discussion.

The writer further desires to introduce with catalysis the induced reaction in which the "catalyst" suffers change in the reaction for it seems that the evaluation of this kind of phenomena would be not only highly arbitrary but misleading as well. For the same reason, the phenomena of induced photochemical and solution will be discussed.

It is of course evident that if a reaction could be found which is catalyzed by a certain element or chemical in a manner not satisfied by other substances, one would infer very small results of the analyst by observing its effect upon the reaction.

I. Catalysis Due to Colloid Formation

1. The formation of "fog" caused by giving off gaseous products slowly at room temperature. This may be also accelerated by the formation of "nuclei" (1,2).

2. Colloids in a medium or "fluid" role addition for only very weak catalytic effects. This addition of a trace of colloid matter is made then known as "negatively catalytic agents". It can be seen that the solubility of CO2 is markedly greater in neutral H_2O, indicates that in water. Further the solution potential of such a solution is much greater than that of a solution of H_2O alone. This has been interpreted as initiative of the formation of a complex H_2O-CO_2 (3, 4, 5).

2. Catalysis Due to Physical Colloid Composite Complexes

a. $H_2O_2 + Na_2S_2O_3 + 2HC_2H_3O_2 = Na_2S_4O_6 + 2NaC_2H_3O_2 + 2H_2O$ but with a trace of $MoO_4^{=}$ (6)

$$4H_2O_2 + Na_2S_2O_3 = 3H_2O + Na_2SO_4 + H_2SO_4$$

The same effect may be achieved with tungstates, vanadates, and zirconium, thorium, and titanium salts (7).

b. $2H_3AsO_4 + 10H^+ + 4I^- = 2As^{+3} + 2I_2 + 8H_2O$

$$2As^{+3} + 3H_2S = \underline{As_2S_3} + 6H^+$$

$$2I_2 + 2H_2S = 4I^- + 2S + 4H^+$$

These reactions of catalytic nature are used in qualitative analysis in order to avoid the slow precipitation of As_2S_5 (8).

c. $2NaN_3 + I_2 = 2NaI + 3N_2$

This reaction is quite slow but very greatly accelerated by $S^{=}$ in many forms (9, 10).

d. The salts of Cu^{++} enjoy the distinction of acting as catalysts in both oxidation and reduction reactions. This is due no doubt to the formation of relatively unstable Cu^{+++} salts in the first case and Cu^{+} salts in the second case.

An example of the use of copper salts as oxidizing catalysts is found in the oxidation of manganous ion to permanganate by hypobromite. Unless a trace of a copper salt is present, manganous dioxide (not permanganate) results (11).

The reaction between the ferric ion and thiosulphate ion ($2Fe^{+++} + 2S_2O_3^{=} = 2Fe^{++} + S_4O_6^{=}$) is very greatly accelerated by a very slight trace of a cupric salt. This reaction illustrates the role of Cu^{+} as a catalyst in reduction reactions (12).

3. Induced Reactions

If a reaction velocity is augmented by the occurrence of another (apparently unrelated) reaction which occurs at the same time as or just before the first reaction, that first reaction is said to be an induced reaction (13).

a. The classical example of an induced reaction is the oxidation of sodium arsenite solution by the oxygen of the air (this reaction proceeds by itself too slowly to be measured) in the presence of a sulphite which is itself being oxidized to a sulphate.

According to the classical nomenclature of Kessler, we may consider this induced reaction in two steps:

$2SO_3^{=} + O_2 = 2SO_4^{=}$ (inducing reaction)

$2AsO_3^{\equiv} + O_2 = 2AsO_4^{\equiv}$ (induced reaction)

Such coupled reactions have a common component (O_2 in this case) called the actor. The material in the inducing reaction which reacts with the actor is called the inductor ($SO_3^{=}$), and the substance which thereby undergoes chemical changes in the induced reaction is called the acceptor ($AsO_3^{=}$). If we define a term called induction factor which is the ratio of oxidized equivalents of the acceptor to oxidized equivalents of the inductor, we may observe that the greater this value becomes the more nearly catalytic the reaction appears to be. Thus, the fields of induced reaction and catalytic reaction tend to merge.

An example of an induced reaction with a high induction factor is the oxidation of oxalic acid by mercuric chloride (in a solution of proper concentration this does not occur at a measurable rate) induced by the oxidation of some of the oxalic acid by permanganate. In the presence of a trace of permanganate a copious precipitate of mercurous chloride is soon formed (14).

4. Induced Precipitation and Solution.

A substance which would not normally precipitate under a given set of experimental conditions will sometimes co-precipitate with another substance. The phenomenon is called induced precipitation. Conversely it is occasionally possible to effect the solution of a substance not normally soluble in a given reagent by simply allowing the reagent to react with a mixture of that substance and another substance soluble in the reagent.

An example of induced precipitation is the crystallization of lead sulphate from solution in acetic acid and ammonium acetate by the formation of a trace of barium sulphate in the solution.

The phenomenon of induced solution is shown by the ability of a solution of dilute nitric and tartaric acids to dissolve completely and rapidly an alloy of tin and antimony. Tin alone gives metastannic acid.

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See also the very excellent discussion of this subject by F. Feigl, Specific and Special Reactions, Elseview Publishing Co., New York, 1940, p. 65 ff.

THE BORON HYDRIDES

Margaret Kramer January 9, 1945

I. Introduction:

About 1810, Davy noticed that the mass obtained in the preparation of boron by reduction of B_2O_3 with potassium when treated with water or dilute HCl produced a gas which was mainly hydrogen, but which has a disagreeable odor and which burned with a blue flame tinged with green. Wohler, H. St.C. Deville (1858), and Moissan (1893), among others, tried to prepare boron hydride by action of dilute HCl on aluminum boride or by direct union, or by other means, but without success(10).

Jones (1879) obtained a mixture of the hydrides by treating magnesium boride with acids. In 1901 Ramsey and Hatfield demonstrated the gas was a mixture of several hydrides condensed by liquid air (13).

From about 1912 until 1931 most of the work on the born hydrides was done by Stock and coworkers (19). Since 1931 other investigators have entered the field, and their further work has resulted in improved methods of preparation for the hydrides as well as an elucidation of their structures.

Since boron is a trivalent element, its simplest hydride should be BH_3. Such a compound has not been isolated, however, the simplest boron hydride capable of independent existence being B_2H_6. In certain chemical reactions B_2H_6 gives evidence of being composed of BH_3 units. Burg and Schlesinger (5) have noted that linkages between boron atoms seldom occur in compounds of boron with elements other than hydrogen. The tendency for such linking is so strong that BH_3 does not exist.

According to older theories of valency, boron should form hydrides of the general formula B_nH_{n+2}(16). The boron hydrides now known are B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. Such a general formula does not apply.

The advent of the electron theory of valency did not at first improve matters. If one assumes B_2H_6 to have an ethane-like structure, 14 valence electrons are required, while B_2H_6 can muster only 12.

The result of this abnormality has been increased research on the boron hydrides, their chemistry and their structures.

II. Preparation:

The first hydride prepared by Stock, using a special technique involving high vacuum and low temperature distillation, was B_4H_{10}. The yield was rather small, and other heavier hydrides of boron were in the reaction product as well (19).

$$6Mg + B_2O_3 \longrightarrow Mg_3B_2 + 3MgO$$

$$Mg_3B_2 \xrightarrow{10\%\ HCl} B_4H_{10} + \text{traces of } B_5H_9,\ B_6H_{10},\ B_{10}H_{14} \quad (26)$$

THE MOON QUESTIONS

Margret Ferrer January 9, 1965

I. Introduction:

About 1950, Dmitri Dmitri found the data obtained in the preparation of boron by reduction of BCl_3 with hydrogen when treated with water or alcohol yield a gas which has melting properties, but which has a disagreeable odor and which burns with a blue flame tinged with green. Wohler, H. Moissan, Ferrie (1890), and Stock (1909), among others, tried to prepare boron hydrides by action of dilute HCl on aluminum borides or by direct union, or by other means, but without success(20).

Jones (1949) obtained a mixture of the hydrides by treating magnesium boride with acids. In 1951 Schott and Wartik dis-covered the gas was a mixture of several hydrides contaminated by liquid air (32).

From about 1952 until 1961 most of the work on the boron hydrides was done by Stock and associates (10). Since 1961 other investigators have entered the field, and their further work has resulted in im-proved methods of preparation for the hydrides as well as in elucidation of their structure.

Since boron is a trivalent element, its atomic hydrides should be BH_3. Such a compound has not been isolated, however, the simplest boron hydride appears of tetravalent existence being B_2H_6, it occurs chemical resistance B_2H_6 have estimate of being compound of BH_3 units. Ring and Schlesinger (9) have noted that liquids between boron atoms which occur in compounds of boron with elements other than hydrogen. The tendency for such linking is so strong that BH_3 does not exist.

According to older theories of valency, boron should form hy-drides of the general formula B_nH_{n+3} (1). The boron hydrides are B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and B_6H_{12}. Such a general formula does not apply.

The advent of the electron theory of valency did not at first improve matters. If one assumes BH_3 to have an octet-like struc-ture, in valence electrons are required, while B_2H_6 can meet only

The result of this discussion has been increased research in the boron hydrides, their chemistry and their structures.

II. Discussion:

The first hydride produced in bulk, using a special technique involving high vacuum and low temperature distillation, was B_2H_6. The yield was rather small, and other hydrides hydrides of boron have in the reaction product as well (32).

$$6NaH + 2BF_3 \longrightarrow B_2H_6 + 6NaF$$

$$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$$

Wiberg and Schuster found that 8N H_3PO_4 increased the yield from about 4% to 11% (28). Upon heating at 100°, the hydride forms B_2H_6 and small amounts of B_5H_9 and $B_{10}H_{14}$ (7).

A second method for the preparation is:

$$B_5H_{11} \xrightarrow[1.5\ atm.]{100°} \underset{85\%}{B_4H_{10}} + B_2H_6 \quad (4)$$

B. B_2H_6 is most simply prepared by action of hydrogen on boron trichloride under suitable conditions (3).

Pure hydrogen is bubbled through liquid BCl_3 at -40°C. and the resulting mixture is passed through a 12-15 kilovolt discharge formed between water cooled copper electrodes. The pressure is maintained between 5 and 10 mm. The products are much unchanged boron trichloride and hydrogen, together with B_2H_5Cl and a small amount of B_2H_6. The mixture is condensed from excess hydrogen and fractionated to remove HCl. At a pressure of 2 mm. at 0°C, B_2H_5Cl decomposes:

$$6B_2H_5Cl \rightleftharpoons 5B_2H_6 + 2BCl_3$$

The diborane is removed as fast as it is formed. Fractions rich in hydrides are further fractionated and the resulting B_2H_6 is finally purified by vacuum distillation at -150°C.

The method may be improved by using BBr_3 instead of BCl_3, the resulting HBr being more easily removed. BBr_3 is less volatile than BCl_3 (22). Yields as high as 80% of the halide reacting have been reported.

C. Other boranes are prepared by heating B_2H_6 under suitable conditions.

$$B_2H_6 \xrightarrow{115°} H_2 + B_4H_{10} + \underset{\text{(Main product)}}{B_5H_{11}} \quad (4)$$

$$B_2H_6 \xrightarrow[180°]{\text{high vac.}} B_5H_{11} + B_4H_{10} \quad (23)$$

$$B_2H_6 \xrightarrow[\substack{250°-300° \\ \text{Hg vapor}}]{120\ mm.} B_5H_{11} + \underset{\text{(Main product)}}{B_5H_9} \quad (23)$$

$$B_2H_6 \xrightarrow[\substack{160°,\ \text{slightly above atmos.} \\ \text{pressure.}}]{\text{sealed tube}} B_{10}H_{14} \quad (19)$$

$$B_4H_{10} \xrightarrow[\text{vacuum}]{90-95°} B_{10}H_{14} \quad (19)$$

B_6H_{10} was prepared by Stock and Massenez (24) in small quantities from the crude gas appearing upon decomposition of magnesium boride with acid,

III. Properties (see table 1):

A. Thermal stabilities

1. B_5H_{11} least stable.

$$B_5H_{11} \longrightarrow B_2H_6 + B_4H_{10} + H_2 + B_5H_9 + B_{10}H_{14} \quad (4)$$

Wiberg and Tompkins found that at $-140°C$, increased the yield from about 40 to 115 (28). Upon heating at $100°$, the hydride form Ta_2H and small amounts of TaH and Ta_3H_4 (7).

A general method for the preparation is:

$$Ta_2O_5 \xrightarrow[1.5\ atm.]{100°,\ 800} Ta_2H_x + H_2O \quad (4)$$

Ta_2H_x is most slowly prepared in region of hydrogen on heating relatively mild reaction conditions (6).

Pure nitrogen is passed through liquid BCl_3 at $-45°C$, and the resulting mixture is passed through a 18-12 stainless steel tubular battery water cooled copper electrode. The pressure is maintained between 0 and 10 mm. The products are much resembling those tricoloride and hydrogen, together with Ta_2Cl_3 and a small amount of BN. The mixture is condensed from excess hydrogen and filtrated to remove HCl. At temperatures of 8 mm. and $0°C$, Ta_2Cl_3 decomposes:

$$6Ta_2Cl_3 \xrightarrow{\text{arcing}} 3Ta_2N + 12HCl$$

The chlorine is removed as $CaCl_2$ in H_2 dryers. Tantalum Ta_2N hydrides are further transformed and the resulting Ta_2N is finally purified by vacuum distillation at $-1800°C$.

The method may be improved by using $TaCl_5$ instead of BCl_3, the resulting HCl being more easily removed. $TaCl_5$ is less volatile than BCl_3 (29). Yields as high as 80% of the metallic reducing are reported.

D. Other ternary nitrides are prepared by heating Ta_2N under suitable conditions.

$$Ta_2N \xrightarrow{1100°} Ta + Ta_2Na + Ta_3N_4 \quad (4)$$
(main product)

$$Ta_2N \xrightarrow[100]{\text{heat}} Ta_2Ly + Ta_2Na \quad (22)$$

$$Ta_2N \xrightarrow[\text{in vapor}]{\text{heat}} Ta_2Ly + Ta_2N \quad (23)$$
(main product)

$$Ta_2N \xrightarrow[\text{pressure}]{\text{heated 100°, slightly above atmos.}} Ta_2Na \quad (24)$$

$$Ta_2N \xrightarrow[\text{vacuum}]{\text{20-100°}} Ta_2Na \quad (25)$$

Ta_3N_4, are invested by Hack and Johnson (24) in small quantities from the nitrogen and hydrogen upon isomorphism of tantalum hydride with acid.

III. Properties (see Table 1):

A. Thermal stability

2. B_2H_6, stable, decomposes at 100° or above.

$$B_2H_6 \longrightarrow B_4H_{10} + B_5H_{11} + B_5H_9 + B_{10}H_{14} \quad (2)$$

3. $B_5H_{10} \xrightarrow[\text{temp.}]{\text{ord.}} B_2H_6 + H_2 + B_{36}H_{56}$ (20)

4. B_5H_9, stable up to 150°. (16)
5. $B_{10}H_{14}$, stable up to 170°. (16)

B. Chemical reactions (16, 19).

1. Oxygen

B_5H_{11} and B_5H_9 burn spontaneously at ordinary temperatures. $B_{10}H_{14}$ explodes at 100°. B_5H_{10} is only slowly affected by air. B_2H_6 and B_4H_{10} react above room temperatures. The products of the reactions are of indefinite composition.

2. Water

The boron hydrides are hydrolyzed by water to produce boric acid and hydrogen.

The mechanisms of the reactions have not been established. Wiberg suggests no less than 10 steps in the reaction of diborance with water. Of the 9 compounds formed, 5 are unknown, and 3 are hypothetical (16, 29).

3. Halogens (19)

Diborane, stable pentaborane, and decaborane react with the halogens to produce substituted boranes.

4. Hydrogen halides (19)

Diborane and tetraborane react with hydrogen halides to produce substituted boranes, The reactions proceed in the presence of aluminum chloride.

Stable pentaborane and decaborane do not react.

5. Ammonia (16, 19).

Under carefully controlled conditions, diborane reacts to produce a diammonia derivative:

$$B_2H_6 + 2NH_3 \xrightarrow{-120°C} B_2H_6.2NH_3$$

For this compound the structures $(NH_4)_2(H_2B::BH_2)$ and

$$NH_4 \quad H_3B:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:BH_3$$

Upon heating, the two products produce $B_3N_3H_6$, with a ring structure.

6. Metals (16)

Sodium, potassium, and calcium react with diborane to give compounds of the type $M_2B_2H_6$, where M is a monovalent metal. B_4H_{10} reacts with sodium. B_2H_5I reacts also with sodium.

$$B_2H_5I + 2Na \longrightarrow B_4H_{10} + 2NaI \quad (25)$$

2. Stable, stable, isocoloury at 100° or above.

$$BaTe \longrightarrow BaTi_2 + BaTi_3 + Ba_2Ti_9 \quad (7)$$

3. $BaTe_2 \xrightarrow{100°} BaTi_2 + Ba + Ba_2Te_3$ (20)

4. Ba_2Ti_9, stable up to 180°. (18)

5. Ba_2Te_3, stable up to 100°. (18)

4. Positive precipitate (12, 19).

1. Copper.

$BaTi_2$ and $BaTi$ react exothermically as spontaneous forces. Ba_2Ti_9 explodes at 100°. $BaTi_3$ is only slightly affected by air. $BaTe$ and Ba_2Te_3 react above room temperatures. The stability of the reactions for at initiation temperatures.

2. Water

The boron hydrides are hydrolysed by water to produce boric acid and hydrogen.

The sodium salts of the reactions have not been established. Where reactions are less than 10 atoms in the position of diffusion with water, of the 3 compounds (cross), 2 are unknown, the 3 are hypothetical (16, 20).

3. Halogens (12)

Iodine, which participates, not particularly reacts may halogens to produce substituted borons.

4. Hydrogen halides (10)

Chlorine and hydrochloric react with hydrogen halides to produce substituted borons. The reactions proceed in the presence of aluminum chloride.

Stable substituents are particularly in that result.

5. Ammonia (12, 19).

Under carefully controlled conditions, ammonia reacts to produce a diammonia derivative:

$$BaTe + 2NH_3 \xrightarrow{-100°C} BaTe.2NH_3$$

For this compound the structure (Ba)[Ba(NH$_3$)$_2$Te] is

$$\text{or} \quad [Ba]^{+}[Ba(NH_3)_2Te]^{-}$$

$$\parallel$$

Upon melting, the two products decompose $BaTe_2$, with a ring structure.

6. Metals (12)

Sodium, potassium, and calcium react with diborane to give compounds of the type MeB_2H_7, where M is a monovalent metal. $BaTe$ reacts with sodium. Metal reacts also with melting.

[illegible]

7. Metallo boronhydrides (6, 15, 17)

These are prepared by action of B_2H_6 on alkyl compounds of lithium, beryllium, and aluminum.

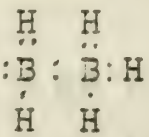
$$2C_2H_5Li + 2B_2H_6 \longrightarrow LiBH_4 + (C_2H_5)_2B_2H_4$$

8. Coordination compounds (8, 16)

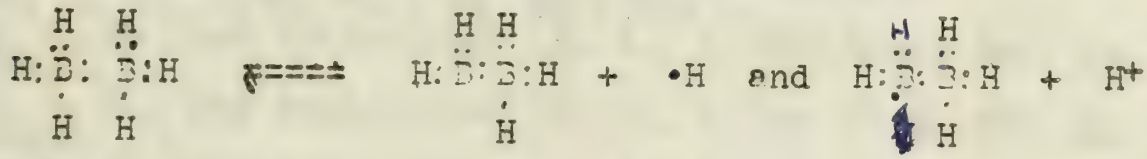
At relatively low temperatures B_2H_6 reacts to produce coordination compounds of borine (BH_3). The following compounds react to form the coordination compounds: $(CH_3)_3N$, CH_3NH_2, $(CH_3)_2NH$, CO, $(CH_3)_2O$, PH_3, CH_3CN, and C_6H_5N.

IV. Structure

A. Sidgwick has proposed single electron bonds in the structure of B_2H_6 (18).

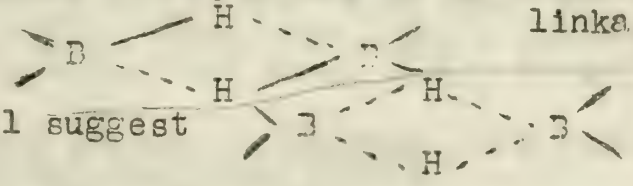


B. Pauling considers such a structure possible under the following conditions: "a stable electron bond can be formed only when there are two conceivable electronic states of the system, with essentially the same energy states differing in that for one there is an unpaired electron attached to one atom and for the other the same unpaired electron is attached to the second atom" (14). Resonance produces a stable molecule.



C. Bauer (2), using electron diffraction methods concludes that diborane has an ethane-like structure, tetraborane a butane-like structure, unstable pentaborane either a pentane- or iso-pentane-like structure. Stable pentaborane was assigned a methylene cyclobutane structure. Hexaborane is said to have a dimethyl-clyclobutane-like structure. Decaborane is said to have a double 4-membered ring with BH_3 groups at the two ends:

D. Nekrasov (11, 12) considers the hydrides to be coordination compounds held together by



linkages.

Longuet-Higgins and Bell suggest linkages (9).

Wagner discounts the ethane structure for diborane, suggesting instead an ethylene-like structure (27).

$$H_2BH_2BH_2.$$

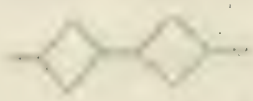


TABLE 1 (16)

PHYSICAL CONSTANTS OF THE BORANES

Name	Molecular Formula	Density	Melting Point	Boiling Point	Vapor Tension
			°C	°C	Mm
Diborane	B_2H_6	0.577(-183°C) 0.477(-112°C)	-165.5	-92.5	225(-119.9°C)
Tetraborane	B_4H_{10}	0.56 (-35°C)	-120	18	388 (0°C)
Stable Pentaborane	B_5H_9	0.61 (0°C)	-46.6	48	66 (0°C)
Unstable Pentaborane	B_5H_{11}		-123	63	53 (0°C)
Hexaborane	B_6H_{10}	0.69 (0°C)	- 65		7.2 (0°C)
Decaborane	$B_{10}H_{14}$	0.92 (99 °C) 0.78 (100°C)	99.7	213	19 (100°C)

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TABLE 1 [10]

SYNTHETIC DISTANCES OF THE SPECIES

Species	Relative Frequency	Density	Relative Basal Area	Relative Point Frequency	Major Terrain
	x_1	x_2	x_3	x_4	x_5
Oliverea	$z_1 y_1$	0.477 (-1.0477) 0.497 (-1.1949)	-1.3	-0.1	1.2 (-1.0)
Tetraodonea	$z_2 y_2$	0.42 (-0.0471)	-1.0	1.0	0.8 (0.0)
Trailia					
Teniadoneae	$z_3 y_3$	0.21 (0.0)	-1.6	.0	0.0 (0.0)
Unrelated					
Tachideae	$z_4 y_4$		-1.0	0.0	0.0 (0.0)
Isadoneae	$z_5 y_5$	0.03 (0.0)	- .0		0.8 (0.0)
Weddoneae	$z_6 y_6$	0.02 (.00 -0) 0.00 (.00-0)	1.7	1.1	1.0 (0.0-)

A SURVEY OF INORGANIC NITRIDES; PROPERTIES, PREPARATION, AND REACTIONS

Lawrence J. Edwards January 16, 1945

I. General Consideration.

The affinity of nitrogen for other elements is not manifested at ordinary temperatures, but on heating combination often occurs. Combination of a metal and nitrogen is usually exothermic, whereas the formation of a non-metallic nitride is the result of an endothermic reaction (23). The formulas of the nitrides, in the cases where they have been definitely established, are usually those which are to be expected from the ordinary valency of the second element and the tri-valency of nitrogen. Consequently, nitrides can be regarded as salts derived from the anhydro-acid ammonia.

II. Various Methods of Preparation and General Properties.

1. Direct Combination.

Generally, direct combination takes place at moderate or high temperatures with the element or amalgams of the element. Thus, Li, Mg, Ca, Sr, Ba, B, Al, Si, Ti, Zn, V, Nb, Cb, Ta, Cr, U, Mn, and some of the rare earths have been prepared by this method. Lithium is rather unique in that it gives the nitride at a red heat (21)(10) and even in the cold (3). Amalgams of the alkaline earths are heated in atmosphere of nitrogen (17). Metallic Lanthanum absorbs nitrogen but sometimes in no definite proportions (20). The nitride of these reactive metals are dark powders easily hydrolyzed by cold water (9)(18). Ti, Ta, Zr, Hf and Cb nitrides conduct an electric current without decomposition and because of their high melting points, they are suitable for arc lamp electrodes or for cathode tubes or discharge tubes (1).

2. The Action of Carbon and Nitrogen on Oxides.

AlN is formed when aluminum oxide, mixed with carbon, is heated to a high temperature in a current of nitrogen. However, this procedure sometimes gives in addition, cyanide and cyanamide (9).

3. The Action of Gaseous Ammonia on Metals or Their Oxides.

When ammonia is passed over cupric or cuprous oxide at 300°C, a nitride, having the composition Cu_3N can be separated (2). However, using zinc dust and ammonia, the product contains less nitrogen than is required by the formula Zn_3N_2 (20). Nitrides of Fe, Ni, and Co give variable compositions (2)(4)(7)(19).

4. The Decomposition of Amides and Imides by Heat.

Each of the intermediate compounds has been isolated, and the conditions of the successive changes determined in the case of arsenic (13).

$$2As(NH_2)_3 \xrightarrow{60°C} As_2(NH)_3 + 3NH_3$$
$$As_2(NH)_3 \xrightarrow{250°C} 2AsN + NH_3$$

A SERIES OF INORGANIC NITRIDES; PREPARATION, PURIFICATION, AND PROPERTIES

Lawrence A. Sylvania January 16, 1943

I. General Considerations.

The affinity of nitrogen for other elements is not meaningful at ordinary temperatures, but on heating combination of nitrogen. Combination of a metal and nitrogen is usually another whereas the formation of a non-metallic nitride is the result of an endothermic reaction [20]. The formulas of the nitrides, in the cases where they have been definitely established, are usually those which are to be expected from the military values of the second element and the tri-valency of nitrogen. Consequently, nitrides can be regarded as salts derived from the nitride-acid ammonia.

II. Various Methods of Preparation and General Properties.

1. Direct Combination.

Generally, direct combination takes place at moderate or high temperatures with the element or analogues of the element. Thus, Li, Mg, Ca, Sr, Ba, B, Al, Si, Ti, Zr, V, Nb, Cb, Ta, Cr, U, Th, and some of the rare earths have been prepared by this method. Lithium is unique in that it gives the nitride at a red heat (23)[12] and even in the cold [1]. Analogues of the alkaline earths are best in atmosphere of nitrogen [17]. Unstable lanthanum nitride appears but sometimes is in definite proportions [20]. The nitride of these reactive metals are dark grayish powders decomposed by cold water (3)[10]. Ti, Ta, Zr, Hf and Cb nitrides conduct an electric current without decomposition and because of their high melting points, they are suitable for arc lamp electrodes or for vacuum tubes or discharge tubes [1].

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AlN is formed when Aluminum oxide, mixed with carbon, is heated to a high temperature in a current of nitrogen. However, this producing reactions give in addition, cyanide and cyanamide [3].

3. The Action of Gaseous Ammonia on Metals or Their Oxides.

When ammonia is passed over oxides or oxygen salts at 300°C, a nitride, having the composition Cu_3N can be separated [2]. However, using zinc dust and ammonia, the product contains less nitrogen than is required by the formula Zn_3N_2 [20]. Mixtures of Fe, Zr, and Co give white compositions [3][4][5][10].

4. The Decomposition of Azides and Imides by Heat.

Each of the intermediary compounds has been isolated, and the conditions of the successive changes involved in the case of sodium [12].

$$NaN(H)_2 \rightarrow NaNH_2 + NH_3$$
$$2NaN(H)_2 \rightarrow Na_2NH + NH_3$$

5. Action of Aqueous Ammonia.

Aqueous ammonia at ordinary temperatures converts the oxides of silver and gold into the explosive nitrides, Ag_3N. Au_3N, and Au_3N_2.

6. Reactions in Liquid Nitrogen.

The nitrides of tin, lead and cadmium have been prepared by passing an electric arc between electrodes of the metals immersed in liquid nitrogen (5)(6).

7. Reactions in Liquid Ammonia.

Double decompositions which occur between halides and amides in liquid ammonia generally yield complex double amides, frequently with ammonia of crystallization (8).

$$BiBr_3 + 3KNH_2 \longrightarrow BiN + 3KBr + 2NH_3$$

8. The Action of Dry Ammonia on Anhydrous Chlorides.

This type of reaction is applicable more to the chlorides of the non-metals, and especially those of Groups five and six of the periodic table.

III. Miscellaneous.

1. Transition vs. Non-Transition Elements.

Hagg (11) found that binary compounds between metals and nitrogen had metallic properties when the metal is a transition element; non-metallic properties are shown when the metal is not a transition element. Klemm and Schuth (14) found similar results from magnetic susceptibilities. In the series of elements from Scandium to Nickel with increasing atomic numbers, the stability of the compounds formed between these elements and nitrogen decreases. In the transition elements, if the ratio of atomic radii (rm/rn) is greater than 1.7, the structure becomes more complex, the smaller the radius of the metal ion (12). Vanadium iron, copper, and tungsten do not absorb nitrogen up to 125°, molybdenum absorbs only a small amount. The absorption of nitrogen begins at 780° for Mg and Ca, at 800° for Al and Cr, at 850° for Mn and at 900° for Ti (28). Mg, Ca, and Al give nitrides with definite formulae, while Ti, Cr, and Mn seem to form solid solutions of nitrogen in the metal.

2. Rate of Reaction and Heats of Formation.

The determination of the rate of reaction, of the formation of a nitride by "direct combination" is based upon the color changes of the metal in contact with the gas (24). By plotting a curve of the known heats of formations of some of the nitrides against the corresponding atomic number, the heats of formation of some of the less easily determined nitrides can be obtained by interpolation (15).

3. Decomposition Pressure and Temperature.

Lorenz and Woolcock (18) measured the decomposition pressure of BN between 1695 and 2045°C. They found the reaction to be reversible and by plotting Log p vs. 1/T, they got a straight line. Similar investigations with

4. Ability of Adsorbing Impurity.

Minerals capable of selective ion-exchange properties for cations of alkali and alkali earth ion-exchange activities, Ag_2S, HgS, and Ag_2Hg.

5. Electronic or Ionic Conduction.

Or either of the ionic and electronic conductivities have been proved by measuring the electron and hole mobilities of the metal sulfides in aqueous solutions (Ch.6).

6. Capacity of Ionic Exchange.

Ionic exchanges which occur between metal sulfides and aqueous electrolyte solutions are closely related to the ability of the metal sulfides. Especially with respect of degradation (Ch.8).

$$\text{Sulfide} + \text{Acid} \longrightarrow \text{Salt} + \text{H}_2\text{S}$$

7. The Ability of the Formation of Polysulfides.

Metal sulfides are easily to be polysulfide ions in the solutions of the non-metals, and especially those of Group 4A- and 6A of the periodic table.

III. Discussion

1. Conditions Vs. Semi-Conductor Density.

Many attempts have been made to correlate between metal and their metal sulfide (semiconductor) from the metal (e.g. ionization energy, electron affinity, electronegativity properties are given the metal is not a transition element). Kimes and Sutton (24) found that, results for comparing semiconductivities in the series of elements from Sulphur to Bismuth with increasing atomic number, the stability of the semiconductor formed between group elements and nitrogen decreases. In the transition elements, it has been so difficult to correlate the semiconductivity. Dr. Mellor said, "... the electronic behaviour cannot be predicted from the metal or the metal ion (1)". Wagner, and Dreyfus, and Dreyfus so too absorb attention in 1957, molybdenum dioxide only a small energy. The stabilization of interstitial sulfide is "Not" for Fe and Co, at low temperature, or, at 800° for Ni and at 1000 for Cu (28). Ni, and Al form sulfides with definite formulas, while Fe, Co, and Mn seem to form solid solutions of sulfides in wide ranges.

2. Rate of Reaction and Rate of Formation.

The experimentation of the rate of reaction, or the formation of a mineral by "Direct combination" is based on the sulfur charges of the metal in contact with the gas (9). By plotting a curve of the sulfur uptake of formations of sulfides of the minerals against the corresponding atomic number, the limits of formation or loss of the less easily formed sulfides can be estimated by interpolation (10).

3. Thermodynamic Properties and Assumptions.

Lewis (14) Jordan (14) attempt to decomposition pressure of FeS in iron and steels. They found the results to be reversible and by plotting log p vs. 1/T, they gave a straight line. Mellor investigations with

yranium and nitrogen indicated the formation of U_5N_4 and U_5N_2. An investigation conducted by Voznesenskii (25) showed that the more simple the composition of the nitride, and the smaller the atomic volume of its nitride, the higher is its decomposition temperature and consequently the more stable it is to the action of various reagents.

4. Phosphorus Chloronitrides.

When an equimolal mixture of phosphorus pentachloride and ammonium chloride are heated together in a closed tube at 150°, a curious series of compounds is formed, the general formula of which may be designated by $(PNCl_2)_n$, where n = 3, 4, 5, 6, 7 and higher (22)(27). All members of this series seem to be non-polar in character. Due to lack of symmetries in $(PNCl_2)_5$ and $(PNCl_2)_7$, these two compounds have remarkably low melting points. This series of phosphorus chloronitrides reacts only slowly even with boiling water. The rate of hydrolysis can be increased by the addition of a little ether to the water. Upon hydrolysis, these compounds yield hydroxy derivatives $[PN(OH)_2]_n$.

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[illegible] [illegible] the formation of D_2O, and D_2O_2. An investigation conducted by Vorsanwill [illegible] showed that the more stable the hydrolysis of the nitrid and the smaller the atomic volume of its nitride, the higher is its thermostatic temperature and consequently the more stable it is to the action of various reagents.

4. Inorganic Chloronitrides.

When an equimolar mixture of phosphorus pentachloride and ammonium chloride are heated together in a closed vessel at 150°, a quantitative yield is obtained, the product formula of which may be derived by $[NPCl_2]_x$, where = [illegible] 3, 4, 5, 6, 7 and higher [illegible]. All members of this series seem to be non-polar in character. The $(NPCl_2)_3$ and $(NPCl_2)_4$ [illegible], these two compounds have proved ably low melting points. This series of phosphorus chloronitrides exists only [illegible] with melting points. The type of [illegible] can be interpreted by the addition of a little water to the [illegible]. Some hydrolysis, these compounds yield [illegible] derivatives [illegible] [illegible]

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ROLL CALL

January 23, 1945

Hydrides of Aluminum and Gallium

Therald Moeller

For many years the boron hydrides have been regarded as unique among the covalent hydrides because of lack of sufficient electrons for the formation of complete series of electron pair bonds. Recent reports of the preparation of a volatile gallium hydride, Ga_2H_6 (1, 2); and a non-volatile polymeric aluminum compound of composition $(AlH_3)_x$ (3) would indicate this phenomenon to be general among at least the beginning members of Periodic Group IIIb.

Preparation of the gallium compound (1, 2) involves reaction of $Ga(CH_3)_3$ with H_2 in a glow discharge to produce $Ga_2H_2(CH_3)_4$ which in turn reacts with $(C_2H_5)_3N$ to give $Ga(CH_3)_3.N(C_2H_5)_3$ and Ga_2H_6. The latter compound solidifies at -21.4°C. and boils, with decomposition, at 139°C.

Preparation of the aluminum compound (3) is similar in that it first involves the reaction of $Al_2(CH_3)_6$ with H_2 in a glow discharge. A complex mixture of volatile and non-volatile components results, from the volatile portion of which $Al_2H_2(CH_3)_4$ can be separated. Treatment of this material with $(CH_3)_3N$ yields $Al(CH_3)_3.N(CH_3)_3$ which, on heating, eventually gives $(AlH_3)_x$, a white, non-volatile solid, stable to 100°C., but decomposing at higher temperatures to Al and H_2.

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ROLL CALL

January 23, 1945

Report on the "Industrial and Electrochemical Conference" held in Chicago, January 19, 1945.

John C. Bailar, Jr.

This conference, sponsored by the Chicago section of the Electrochemical Society, was designed to convince businessmen of the possibilities for a postwar electrochemical industry in the midwest. The early talks dwelt on Chicago as a manufacturing center and on its power supply.

Dr. Harold Vagtborg, President of the Midwest Research Institute, predicted the growth of many such institutes to serve the smaller companies that can't economically have research laboratories of their own. According to him, there are less than 3000 companies in the United States which are doing research, although there are 180,000 which might well undertake research programs. Before the war, 0.5% of our national income was spent on research, but the Russians were spending 1% of their national income.

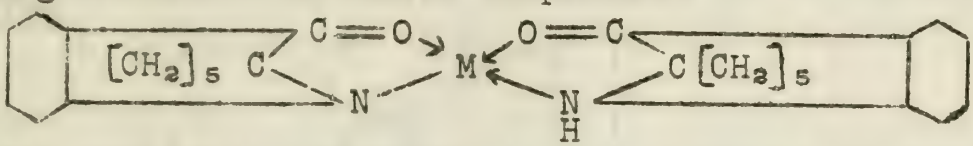
The outstanding talk of the conference was given by R. B. Wittenberg of the International Minerals and Chemical Corporation. He spoke of the five M's of the chemical industry -- management, money, men, markets, and materials -- and told of the importance of each in locating a new chemical industry. The first two are relatively unimportant in this regard. The chemical industries do not require a great quantity of labor, but the quality must be high, so new industries should be located where intelligent, educated labor is available. Markets and materials, of course, play a large role, and may well be determining factors. Even in an electrochemical industry, power may be of secondary importance.

This conference has been described in some detail in Chem. and Eng. News. 23, 238 (1945).

ADDITION COMPOUNDS OF THE ALKALI METALS AND THEIR STRUCTURES

Hans Jonassen February 20, 1945

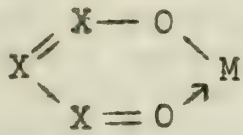
One of the outstanding properties of the alkali metals is their extremely slight tendency to form complex ions. One of the first coordination compounds of these metal ions is reported by Perkin and Plant (1) who isolated a sodium derivative of indoxylspiro cyclopentane. Sidgwick and Plant (2) continued this investigation of alkali complexes with indoxylspiro cyclopentane. They succeeded in isolating an unstable derivative with lithium and stable derivatives with sodium and potassium and assigned the following structure to these complexes:



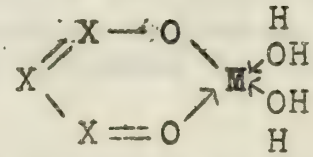
All these complexes decompose in the presence of excess water.

Sidgwick and Brewer (3) extended this work; they were able to prepare numerous solid alkali derivatives with organic molecules containing two electron donor groups. They divided these compounds into four groups with the following structures. X = C or N

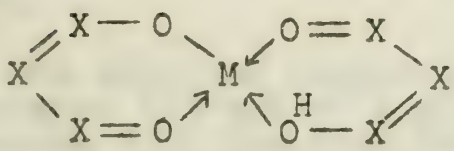
(I)



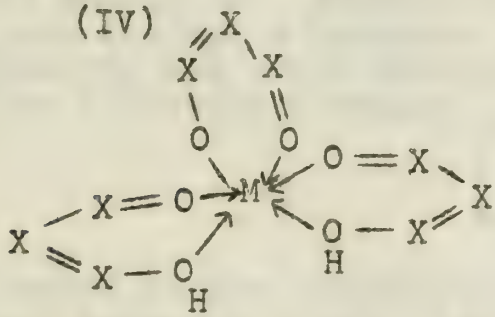
(III)



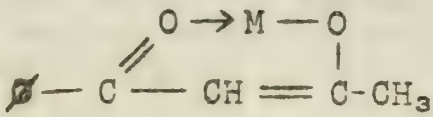
(II)



(IV)



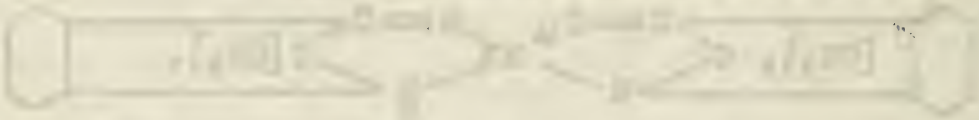
These authors state in their discussion that compounds having structure I are true salts since they show no definite melting points and since they are insoluble in nonhydroxylic solvents. A typical compound of this group is the sodium salt of benzoyl acetone:



ACTIVITY COMPARISON OF THE ALKALI OXALATE AND TARTRATE COMPLEXES

Mary Lowman February 20, 1948

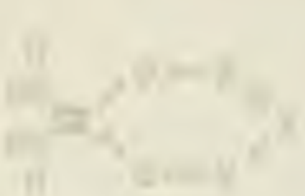
One of the outstanding properties of the alkali metals is their extremely alert reactions in lower organic media. One of the first qualitative comparisons of their order here is reported by Kraus and Kraus (1) who included a qualitative activity of solvolysis with methanol. Kraus and Kraus (2) continued this investigation of alkali ion-lower-alkyl carbonyl compounds. They concluded in looking at qualitative activity with ethanol and acetic derivatives with methanol and ethanol and measuring the following activity in order-of-magnitude:



All lower carbonyl derivatives in the presence of excess metals.

Kraus and Lowman (3) consider this order, but were able to prepare-lowmers with alkali derivatives with organic solvents containing the alcohol ions groups. The activity these compounds have that groups with the following structures. X = 1 or 2

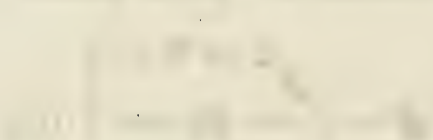
(I)



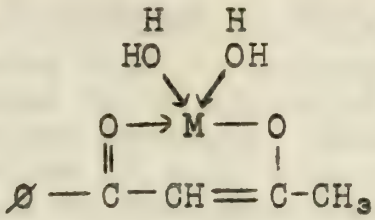
(II)

(IV)

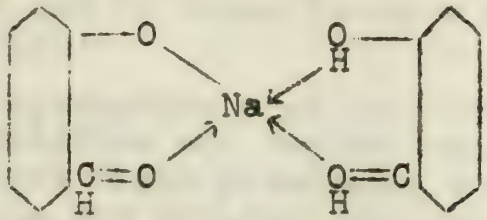
Their initial aims in this alkali-alkali that compounds (III) structures I and II are very alert (low-order in activity solvolysis) while all other that are inactive in comparability solvolysis. A further comparison also based on the active ion of lower order:



Compounds having structures II, III, and IV are coordinate covalent compounds since they are soluble in organic solvents and show definite low melting points. Typical compounds of these groups are the dihydrated sodium salt of benzoyl acetone:



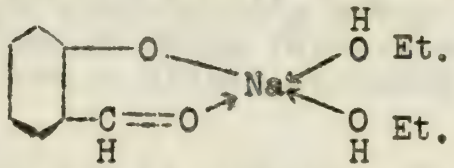
and the addition compound of sodium and two salicylaldehyde molecules



Brewer (4) extended this work to include the most active alkali metal ions cesium and rubidium. He prepared several new addition compounds of these ions with organic molecules, especially salicylaldehyde. In his conclusion Brewer gives a tabulation of all the important addition compounds of the alkali metal ions. The most important contribution of Brewer is that he was able to show that the coordination number of the alkali metals increases in these compounds as would be expected from the increase in their ionic sizes.

The addition compounds of β-alanine prepared by King and Rutherford (5) are of a slightly different type since in these complexes both the positive alkali ion and the negative ion add.

Brady and Badger (6), extending the work of Sidgwick, found that in absolute alcohol a compound is formed between sodium ion and salicylaldehyde and ethyl alcohol molecules; they tentatively assigned it the following formula:



In the course of dye investigations, Brady and Porter (7) were able to prepare extremely stable addition compounds of all the alkali metal ions with 4-isonitro-1-phenyl-3-methyl-5-pyrazolone. These compounds are extremely stable in water, soluble in organic solvents.

Hogson and Batty (8) continued this work and reported the isolation of sodium addition compounds with 2-nitroso-5-methoxyphenols and with some of their substituted derivatives.

During their investigations of the structures of di-2-hydroxy-1-naphthyl sulfide and the corresponding methane, Smiles and coworkers (9,10,11,12) were able to isolate hydrated alkali derivatives of these compounds. Due to its theoretical interest

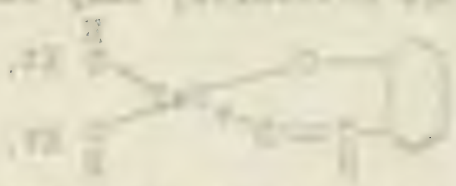
Compounds having structures II, III, and IV are derivatives of compounds which they are active in organic solvents and with deflate lin quinine potato. Typical compounds of these groups are the diphenyl sulfide salt of lauryl sorbate:

and the dialkyl compound of sulfone and the sulfinylphenyl sulfoxide

Brewer (4) extended this work to include the most active mixed ions having sulfur and phosphorus. He prepared several new sulfinyl compounds of these ions with organic moieties, especially sulfinyl alkylsulfide. In this monograph Brewer gives a tabulation of all the important sulfinyl compounds of the alkali metal ions. The most important contribution of Brewer is that he was able to show that the conductivity factor of the alkali metals increases in terms comparable as would be expected from the increase in their ionic sizes.

The addition compounds of polyoxyethylene prepared by Eley and Hutchinson (5) are of a slightly different type since in these compounds both the positive alkali ion and the negative ion add.

Eley and Hedger (6), extending the work of Hedger, found that in alkalate alcohol a complex is formed between sulfur ion and sulfinylalkyle and ethyl alcohol molecules; they tentatively assigned it the following formula:



In the course of his investigations, Eley and Hedger (7) were able to prepare extremely stable sulfinic complexes of all the alkali metal ions with 4-(methylsulfinyl)-2-(2-methoxy-4-methyl-5-methylphenyl)-5-methylphenol. These complexes are extremely stable in water, soluble in organic solvents.

Tuman and Eely (8) continued this work and reported the initiation of anions addition compounds with 2-nitrile-2-methylpropanol and with some of their alkylated derivatives.

During their investigations of the structures of di-2-(2-methoxy-4-methyl) sulfine and the corresponding sulfone, Eely and Hedger (9,10,11,12) were able to isolate hydrated alkali derivatives of these compounds. Due to the theoretical interest

this work was extended to include substituted benzenehydroxy sulfides and related compounds.

Discussion of Structure

In all these papers and the subsequent reviews (13, 14) these compounds are considered to be chelated inner complex compounds with coordinated covalent linkage. However, many experimental facts cannot be explained if such simple linkage is assumed. Most experimental facts seem to indicate that the linkage in these addition compounds is much more complex. They seem to indicate that the linkage in these compounds is ion dipolar rather than coordinate covalent. A few of these facts which seem to substantiate this are given below:

(1) Benzoylacetone does not form addition compounds with potassium, rubidium and cesium because their relatively large radii decrease their polarizing powers.

(2) Sodium and lithium form tetrahydrates with 2-di-hydroxy-1-naphthyl sulfide, selenide, and methane whereas potassium and rubidium only form dihydrates.

(3) In the benzene hydroxy sulfides alkali addition compounds are formed only when the 6 methyl group is present. Since the methyl group is an electron repelling group this increases the electron density in the 1 position. This, in turn, increases the attraction of this position for the hydroxylic proton, which then favors the ketonic form of the benzene hydroxy sulfide. If the alkali derivative formed were purely coordinate covalent it would make little difference whether the ketonic or enolic form were present, because in both cases unshared electrons are present in the outer orbit of the oxygen atom. If, however, ion dipolar linkage is involved the ketonic form should form a much more stable form because its dipole moment is much larger. There is, however, a further factor which has to be considered in the formation and stability of these compounds -- the size of the cation and the distances between the coordinating group in the molecule which adds. A consideration of these factors explains for example, why lithium does not form a stable compound with indoxyl spiro cyclopentane.

Sidgwick's statement that solubility in organic solvents is a criterion for covalency is not necesssrily valid. It can also be explained if a "lock and key" arrangement is assumed similar to that mentioned in Glasstone's article on intermolecular complexes (15). If such an arrangement is assumed, the inorganic part of the molecule would be completely hidden by the much larger organic molecules surrounding it. This explains also why compounds having structure I (cf. p. 53) are insoluble in organic solvents whereas compounds having the other structures are soluble.

The experimental facts discussed in the above part seem to indicate quite clearly that the linkage in the addition compounds of the alkali metal ions with organic molecules containing two electron donor groups is not as simple as maintained by Sidgwick.

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ADSORPTION AND SURFACE IONIZATION ON TUNGSTEN

C. R. Keizer March 6, 1945

I. Introduction
  A. Definitions
    1. Adsorption--the process in which molecules or atoms of a gas or vapor become more or less firmly bound to the surface of a solid.
      a. adsorbent--the solid upon which the adsorption takes place.
      b. adsorbate--the gas which is adsorbed.
    2. surface ionization--the process in which molecules or atoms of a gas or vapor are ionized under the proper conditions upon contact with a solid surface.
  B. Properties of tungsten which account for its use as the most common adsorbent (1, 2, 3, 4)
    1. in powder form
      a. available in rather pure, uniform samples or easily prepared by reduction of the oxide
      b. high sintering temperature permits reduction and degassing at 750° without irreversible alteration of the surface structure.
    2. in the form of filaments or wires
      a. easily cleaned--heating electrically (flashing) to a very high temperature for a few seconds frees surface from all contamination and eliminates gases from interior.
      b. temperature may be easily measured
        1) current-voltage characteristics (5)
          lead-loss corrections (6)
        2) optical pyrometer (7)
      c. stable at high temperatures--can be heated in vacuum for considerable periods of time even at 3000° K., at which temperature all other substances vaporize.
      d. electron emission serves as a sensitive indicator of the presence of adsorbed films. (8)
      e. temperature may be easily and rapidly changed.
      f. chemical stability
      g. other properties not as directly applicable
        1) vacuum-tight seals to glass
        2) strength
        3) ductility
        4) connections to other metals

II. Adsorption (9, 10)
  A. Types of adsorption
    1. physical adsorption--weak interaction between solid and gas; essentially surface condensation; also called van der Waals, low temp. and secondary adsorption.
    2. chemical adsorption (chemisorption)--strong interaction between solid and gas; essentially surface reaction; also called activated, high temperature and primary adsorption.

B. Experimental Methods
  1. Measurement of amount of adsorption
    a. direct
      1) volumetric
      2) gravimetric
    b. indirect
      1) thermionic emission
      2) photoelectric emission
      3) reflection of polarized light
      4) accommodation coefficient
      5) contact potential
      6) electron diffraction
  2. Measurement of specific surface of adsorbent
    a. chemical
    b. physical
    c. optical
    d. electrical
  3. Measurement of heat of adsorption
  4. Presentation of data
    a. isotherm
    b. isobar
    c. isotere
C. Experimental Observations and Deductions
  1. on gases
    a. Langmuir and co-workers (8, 11, 12)
      1) used bulb method, W filament at 1500° K.
      2) hydrogen decomposed to H atoms, which were adsorbed on surface of bulb
      3) oxygen formed WO_3 which evaporated from filament
      4) with mixture of H and O, O disappeared first, then H. Oxide film prevented dissociation of hydrogen molecules.
      5) nitrogen and carbon monoxide formed films similar to oxygen and hydrogen films.
      6) second layer of gases adsorbed at higher pressures
      7) Condensation-Evaporation theory developed to explain these observations.
    b. Roberts (13, 14)
      1) used accomodation coefficient for Ne as measure of adsorption
      2) found filament immediately covered with film of H when exposed to the gas
      3) similar chemisorbed layer of oxygen, stable up to 1700°C. and second layer unstable above 60°
    c. Frankenburger and Hodler (15)
      1) isotherms for hydrogen, nitrogen and ammonia adsorption on W powder--each formed monolayer.
      2) in mixtures, adsorption uninfluenced by presence of other gases
      3) assumed imide and nitride formation as intermediates in decomposition of ammonia

d. Frankenburg (16)
1) studied hydrogen adsorption on W powder over wide range of temperature and pressure
2) found saturation only at high pressures
3) differential heats of adsorption calculated by Clausius-Clapeyron equation
4) at slight coverage H was assumed to be adsorbed as single H atoms; otherwise as molecules
5) heat of adsorption found to be sharply dependent on extent of coverage; explained by
a) heterogeneous nature of W surface
b) differences in state of adsorbed H.

1. for metals
a. Cs studied by Langmuir and associates (8, 12). These studies led to the recognition of the phenomenon of surface ionization.
b. Becker (17) also studied Cs and Ba and Th.
1) for Cs slight coverage at high temperatures.
2) more Cs adsorbed at lower temperatures.
3) thermionic emission a maximum with surface just covered with monatomic layer.
4) at still lower temperatures, still more Cs adsorbed but emission decreases.

D. Surface Migration--lateral motion of adsorbed molecules or atoms over the surface on which they have been adsorbed.
1. Bosworth (18) studied mobility of Na on W strip filament
a. measured photoelectric properties of surface
b. found limit to the capacity of the strip to adsorb Na.
c. excess Na stable on surface, spreads or migrates
d. strip becomes uniformly active in one or two hours at 300° K or 5-10 seconds at 800° K.
2. Becker (19) investigated Ba on W filament
a. measured thermionic emission
b. Ba deposited on one side of W strip, mounted as filament in thermionic valve
c. emission from bare side was found to increase; that from covered side found to decrease until rates were equal.

III. Surface Ionization
A. Metal vapors
1. first recognized by Kingdon and Langmuir (20) while studying the thermionic properties of W filaments coated with caesium; later (21) they found the extent of ionization to be dependent on the condition of the tungsten surface and developed a theory based on the Saha equation (22)
2. confirmatory and supplementary observations
a. Ives (23) Cs on W
b. Becker (17) Cs on W, W-O
c. Killian (24) Rb, K on W--like Cs
d. Meyer (25) K on W, Mo, Ta

e. Althertum, Krebs, and Rompe (26) studying Na and Cs on W, Re found that the temperature dependence of yield of Na^+ from W agreed with theory but yield of Cs^+ fell below theoretical value.

f. Morgulis (27) found that the yield of Na^+ agreed with theory at pressures in range 10^{-3} to 10^{-5} mm. Hg; at lower pressures secondary effects caused disagreement.

g. Mayer (28) studying K on Pt and W found yield of K^+ lower than that predicted by Langmuir-Saha theory.

3. studies at higher temperatures (up to 2700° K) using molecular beam method--Copley and Phipps (29, 30).

B. Metal halides

1. first observed by Rodebush and Henry (31).
2. Phipps and co-workers investigated positive ions
   a. KCl with Copley (32) and Hendricks and Copley (33)
   b. NaCl with Johnson (34)
   c. $BaCl_2$ with Arnett (35)
3. NaCl, KCl, and CsCl were studied by Dukelsky and Yonov (36), who were interested in the negative ions produced.

C. Halogens

1. Mayer with Sutton (37) studied iodine; with Mitchell (38) studied chlorine.
2. Yonov (39) has developed a theory, similar to that of Langmuir, for the case in which a halogen atom leaves the metal surfade as a negative ion.

IV. Applications

A. Theory of surface forces of solids.

B. Mechanism of heterogeneous catalysis (40, 41).

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7. Alderdice, Schale, and Haury (10) studied the and vs as a function of temperature, dependence of yield of "a" from 9 hours, with theory for yield of "a" for this binary diffusion value.

8. Wagenfuhr (97) found that the yield of "a" agrees with theory of presumes in fusion up to 12-fold mm. Hg; at lower pressures monitoring effects reduced significantly.

9. Haury (98) studied K on Zn and I fusion yield of "a" lower than predicted by impulse-theory.

10. Studies of binary isotopicmixtures (by in study" of) with molecular beam methods-Ogden and Ramsey (99).

11. Metal melting.

1. First observed by Johnson and Henry (100).

2. Filippo and co-workers (investigated melting (ice

a. Bill with Cooley (101) and Dewalt and Cooley

b. Bell with Johnson (102)

c. Bell, Wiik, Ajzay (103)

3. Bell, Wiik, and Bell were studied by Dainsky and Ziner (104), who were interested in the computing [illegible] products.

12. Malaysia.

1. Meyer with Rolins (105) studied iodine, with [illegible] (106) studied iodine.

2. Ziner (107) was developing a theory, similar to that [illegible], for the case in which a halogen atom [illegible] the metal surface at a negative site.

IV. Applications.

1. Theory of electron forces of solids.

2. Mechanism of astrophysics materials (40, 41).

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THE STRUCTURE OF LIQUIDS

W. E. Morrell March 13, 1945

What is the arrangement of molecules in a liquid? Is it random, as in gases? Does it resemble the ordered arrangement found in crystals, being either microcrystalline (containing tiny but almost perfect crystals) or quasicrystalline?

The simplest approach to the problem is through the consideration of pure liquids composed of non-polar and practically spherical molecules. Such an approach avoids problems of orientation, whether caused by the shapes of the molecules themselves or by dipoles, and avoids the complications that would accompany the presence of more than one species of molecule.

The structure of a liquid containing a single species of spherical, non-polar molecule can be expressed in terms of a probability or distribution function W (often called g(r) or $\rho(r)$). W "is a measure of the statistical density of molecules at a distance r from any given molecule". $4\pi r^2 W\,dr$ "is hence the probability of finding a molecule within a distance r to r + dr of a given molecule" (4), or it is the average number of molecules around the reference molecule in a spherical shell of radius r and thickness dr. The total number of molecules within distance r of the reference molecule is therefore $4\pi\int_0^r Wr^2 dr$

"The distribution function uniquely characterizes the molecular configuration of a liquid" (4). All that remains to be done is the evaluation of W, the distribution function.

Several methods of evaluationshave been tried. A general idea of the way W varies with r can be obtained intuitively. Mathematical derivations are difficult, and have, in general, yielded only approximate results (1-9).

Experimental evaluations have in general involved (1) x-ray diffraction, or (2) the use of models.

The first satisfactory evaluation of the distribution function were obtained by means of x-ray diffractions in mercury, gallium, and CCl_4 by Debye and Menke (16). Their calculations are based on equations derived by Zernike and Prins (15).

Various kinds of models have been used. Menke (17) poured steel spheres repeatedly onto a flat plate. and measured and tabulated the distances between two black spheres. Prins (10) poured seeds onto a glass plate, photographed them, and from measurements obtained from the photographs, tabulated the relative frequencies of occurrence of the various distances between seeds.

Morrell and Hildebrand (11) used three dimensions instead of two by photographing solid gelatin spheres suspended in a liquid gelatin medium and thereby duplicated Menke's curve for mercury. (Therefore, the atoms in mercury are arranged much like oranges in a pile haphazardly dumped into a grocer's store window. The oranges in the pile show somewhat more regularity or order than do the atoms in mercury, however, as the weight and lack of motion of the oranges causes them to pack relatively more tightly). Stuart and Kast (12,13,14) went back to two dimensions and photographed small discs shaken on a glass plate. They added the effect of dipoles by attaching magnets to the discs.

While the use of models has been helpful, the most fruitful approach is now through the diffraction of x-rays. By this means, the distribution functions of quite a number of liquids have been obtained (15-26). It has been shown that twelve atoms are adjacent to each atom in liquid mercury (16,17), but in liquid potassium each atom is directly surrounded by only eight (22). Lead and bismuth, although they differ in crystal structures, have identical liquid structures (20). Neighboring plate-shaped molecules (e.g. benzene) tend to have flat sides parallel (26).

Long molecules (e.g. hydrocarbon chains) tend to form "cybotactic" groups, small groups of molecules with similar orientation. (Many references by G. W. Stewart and coworkers.)

The hydrogen-bonded, sponge or net-work like structure of water is now, of course, well known, and was elucidated by aid of x-ray diffraction measurements (18,23).

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INORGANIC BENZENE

(Egon Wiberg, University of Munich)

T. G. Klose March 20, 1945

I. Introduction

The compound $B_3N_3H_6$ has been named triborine triamine, borazol and "inorganic benzene".

Stock and Pohland were the first authors to mention borazol and to study its properties to any extent. Their preparative method is still in use and gives a good yield of the compound.

$$B_2H_6 + 2NH_3 \xrightarrow[\text{sealed tube}]{200^\circ} 2BNH_2 + 4H_2$$

The compound was shown by the vapor density method to consist of three empirical units, thus giving the formula $B_3N_3H_6$. Stock and Pohland also showed that the compound was quantitatively hydrolyzed by hydrochloric acid:

$$B_3N_3H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 2NH_3 + 3H_2$$

The greatest yield of "inorganic benzene" thus far reported is 41%, which was obtained by heating ammonia and diborane in the theoretical ratio of 2:1 for forty-five minutes.

II. Constitution of $B_3N_3H_6$.

This compound may have any one of several hundred possible formulas with straight and branched chains or rings. Structures containing the B-B bond are eliminated since they would be too unstable to meet the physical properties of inorganic benzene. This limits the compounds with an empirical formula of $B_3N_3H_6$ to less than a dozen.

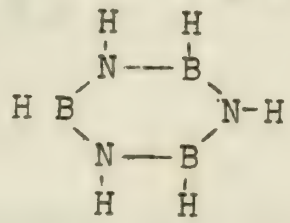
The decision as to the correct formula was made by studies on the two trimethyl substitution products of inorganic benzene $B_3(CH_3)_3N_3H_3$ and $B_3N_3(CH_3)_3H_3$. Most of the trimethyl substitution products have been prepared by Schlesinger, Horvitz and Burg who suggested a mechanism for their formation.

A hydrogen atom was found to be attached to each boron and nitrogen atom by a study of the hydrolysis of the isomeric trimethyl benzenes:

$$B_3N_3(CH_3)_3H_3 + 9HOH \longrightarrow 3B(OH)_3 + 3NH_2CH_3 + 3H_2$$

and $$B_3(CH_3)N_3H_3 + 6HOH \longrightarrow 3CH_3B(OH)_2 + 3NH_3$$

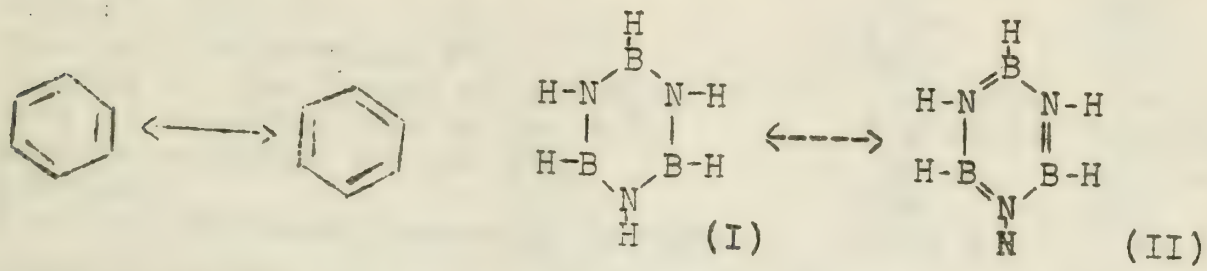
The only structural formula which is possible in light of these hydrolytic properties is:



Stock and Pohland have pointed out that such a "benzene formula" is consistant with all the experimental observations.

Bauer has made diffraction patterns of $B_3N_3H_6$ and found them to correspond almost exactly with diffraction patterns of benzene.

The borazol molecule may exist in one of two possible forms or it may resonate; as with benzene:

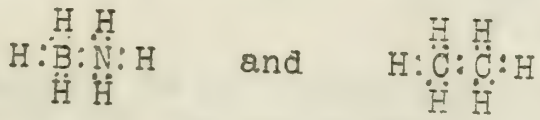


Wiberg reports that the calculated parachor for molecule (I) would be 195 and the calculated value for (II) 260. The experimental value was found to be 208. It thus appears to be in resonance forms.

There are other cases besides "inorganic benzene" in which the C-C pair is substituted with the B-N pair with a remarkable retention of chemical and physical properties.

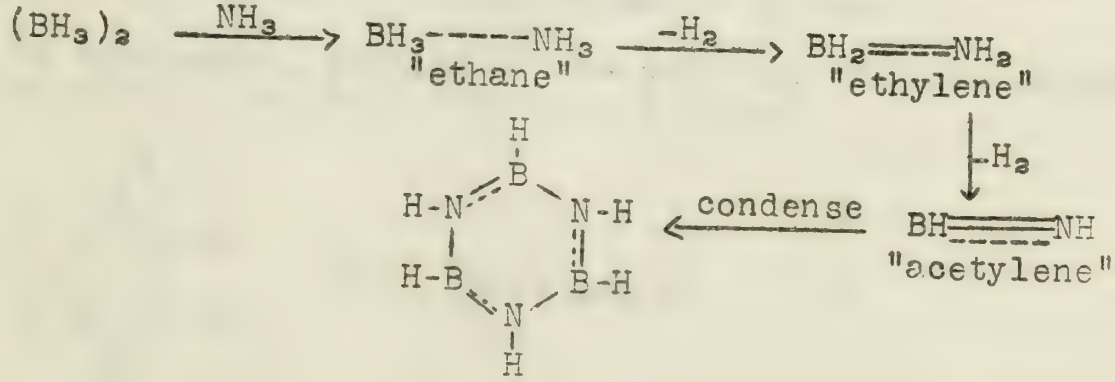
Boron nitride ("inorganic graphite") is analogous to graphite. In fact, two adjacent C-atoms may be replaced with B-N without changing the atomic distances in the lattice.

Ethane and BH_3NH_3 show a close similarity also, as could be predicted from their electronic configurations:



III. Mechanism.

Wiberg's suggested mechanism:



IV. Physical Properties.

Inorganic benzene, like benzene, is a colorless, mobile, inflammable liquid with good solvent properties and a characteristic aromatic order.

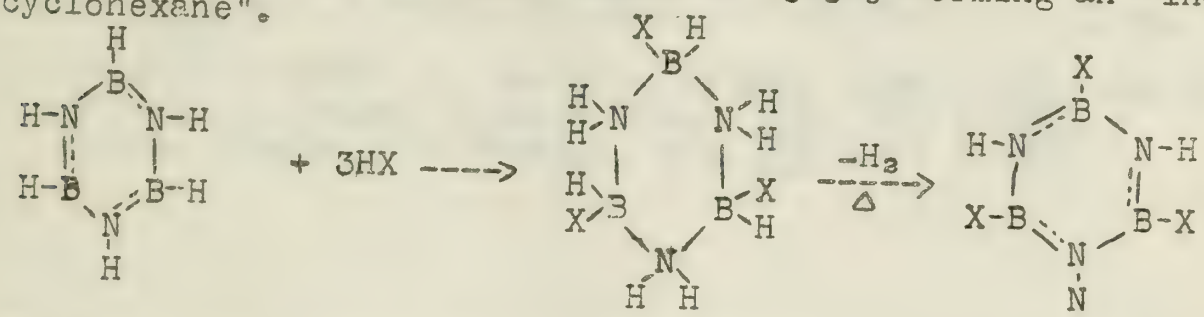
Summary of Properties

	Organic Benzene	Inorganic Benzene
Molecular weight	78	80
Boiling point K°	353°	328°
Melting point K°	279°	215°
Critical Temperature K°	561°	525°
Density of the liquid at the B.P.	.81 g/cc	.81 g/cc.
Heat of vaporization at the B.P.	7.4 Kcal.	7.0 Kcal
Molecular volume at the B.P.	96 cc.	100 cc.
Parachor	206	208
C <----> C distance; B <----> N distance	1.42 Å	1.44 Å

V. Chemical properties.

Inorganic benzene is slowly hydrolyzed at room temperature. A fresh solution of the compound acts as a reducing agent on such ions as MnO_4^- and Cu^{++}.

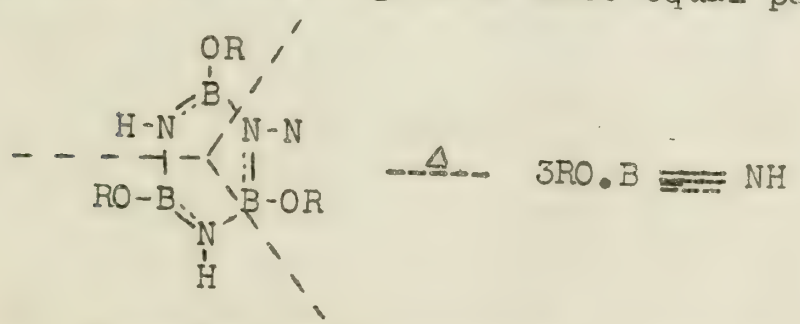
Three moles of a compound of the formula HX (HCl, HBr, HOH, $HOCH_3$) add to the 3 double bonds in $B_3N_3H_6$ forming an "inorganic cyclohexane".



This reaction is not rapid and doesn't appear to be salt formation between HX and the imino group -NH-.

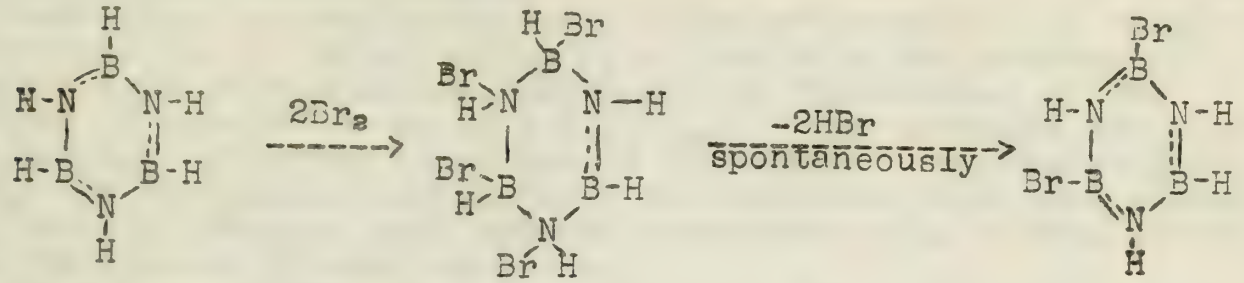
Heating the "cyclohexane" at 50-100° causes the splitting out of H_2 and the formation of the aromatic system.

In some cases, heating of the addition compound causes fission of the ring into three equal parts:



Catalytic hydrogenation of $B_3N_3H_6$ failed to yield a "hexahydrobenzol".

Bromination of "inorganic benzene" leads to the "m-dibromo benzene" whereas with C_6H_6, the p-dibromo compound results:



The hydrolysis product of the dibromo compound is volatile with steam and is thought to be "inorganic resorcinal".

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ROLL CALL

March 27, 1945

Behavior of Metals in Nitric Acid — C. R. Keizer

According to electrochemical theory of corrosion of metals the anodic reaction is relatively simple involving the passage of metallic ions into solution, which may be represented by the equation $M \longrightarrow M^{n+} + ne$ ($n = 1,2,3...$). The cathodic reaction is more complex involving reduction of the reagent surrounding the metal. In the case of nitric acid two reactions are most probable, one yielding hydrogen upon reduction and the other nitrous acid, which decomposes in acid solution.

There is evidence that the reduction of nitric acid to nitrous acid is autocatalytic. Three possible steps in reduction of nitric acid are these:

(1) $HNO_3 + H^+ + e \longrightarrow NO_2 + H_2O$
(2) $NO_2 + H^+ + e \longrightarrow HNO_2$
(3) $HNO_2 + H^+ + e \longrightarrow NO + H_2O$

(1a) $NO_3^- + 2H^+ + e \longrightarrow NO_2 + H_2O$
(2a) $NO_2 + e \longrightarrow NO_2^-$
(3a) $NO_2^- + 2H^+ + e \longrightarrow NO + H_2O$

The author considers (2a) a very probable reaction since it involves only two particles. One British chemist thinks that NO_3^- and NO_2^- are not powerful oxidizing agents but that HNO_3 and HNO_2 are; this would favor (1) and (3) over (1a) and (3a). HNO_2 produced by (2) or (2a) rapidly regenerates NO_2 by the reaction

(4) $HNO_2 + HNO_3 \longrightarrow 2NO_2 + H_2O$

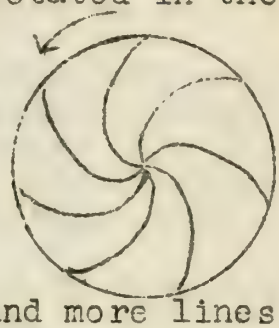
Once a trace of NO_2 has been formed, the reduction of HNO_3 proceeds more and more rapidly.

Highly reactive metals such as Mg, Zn, or Cd generally produce hydrogen or compounds containing it (NH_3, NH_2OH, N_2H_4). In this case the anodic attack is sufficiently rapid to produce a cathodic current density capable of maintaining the formation of hydrogen.

With noble metals (Ag, Cu) the reduction produces nitrous acid (eventually NO or NO_2). It has been found that the presence of urea in the solution represses the attack of the metal. This is explained by the fact that urea reacts with nitrous acid. On the other hand, urea was found to have no effect on the attack of Mg. It has been observed that the attack of HNO_3 on noble metals is most rapid at cracks and crevices where HNO_2 could accumulate. Stirring was found to slow down the action presumably because of removal of HNO_2 from the surface of the metal.

Rotation of a metal disc in HNO_3 was found to increase the rate of solution of Sn, Zn, Mg but to decrease the rate for Ag, Cu. Urmanczy obtained some interesting results when he rotated discs of Ag, Cu, and Zn in HNO_3 solution. For Ag he found that with HNO_3 of concentration less than 4M no weighable amount of Ag was dissolved in 20 minutes, the sample being rotated 220 x per minute. With increasing concentration of HNO_3 the Ag dissolved more and more rapidly. Slower rotation was found to increase the rate of solution of Ag.

Upon examination of the metal discs after being rotated in the HNO_3 he found unique patterns. These he interpreted as indicating that the rate of solution of Ag in HNO_3 is affected by the presence of NO_2. As the bubbles of NO_2 are formed they move out toward the edge of the disc due to centrifugal force. In passing along the surface of the metal they accelerate corrosion at each spot momentarily. These lines were found to be always bent according to the direction of turning the disc. At a higher rate of rotation he found more lines but they were not as deep as those found with lower rates of rotation. This is explained by the fact that the gas is not removed as rapidly when the disc is rotated more slowly.



Copper was found to give patterns similar to those obtained with silver. With zinc no lines were found -- which might be expected. The Zn being very reactive dissolves very rapidly and the catalytic effect of HNO_2 or NO_2 would not be noticeable.

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ROLL CALL

H. A. Laitinen

I. Removal of oxygen from commercial tank nitrogen.

A. The common method of passing the nitrogen over copper turnings or gauze heated to temperature of 450-600° is limited in efficacy by the thermal decomposition of cupric oxide. The use of activated copper dispersed on fuller's earth is superior, since a temperature of 200-250° can be used. Finely dispersed copper oxide is prepared by dissolving basic copper carbonate in concentrated ammonium hydroxide, suspending the fuller's earth in the solution, evaporating to dryness and heating to 180°. The copper oxide is reduced by hydrogen at 200-250°.

Reference: Meyer and Rouge, angew Chem. 52, 637 (1939).

B. Chromous chloride solution can be used for the efficient absorption of oxygen. Lightly amalgamated zinc in a hydrochloric acid solution keeps the chromium reduced to the chromous condition.

II. Sensitive Methods for Analysis of Oxygen in Gases.

A. Probably the most sensitive method known is based on the measurement of phosphorescence which is caused by the presence of oxygen.

Reference: Pollack, Pringsheim and Terwoord, J. Chem. Phys. 12, 295 (1944).

B. The Pauling meter, based on the paramagnetism of molecular oxygen, has not yet been commercially perfected although it has been under development for some time.

C. An electrolysis method based on diffusion of oxygen through a porous graphite cathode is being commercially developed. The oxygen depolarizes the cathode and an electrolytic current proportional to oxygen content of the diffusing gas mixture is observed.

ROLL CALL

A NEW PERIODIC TABLE

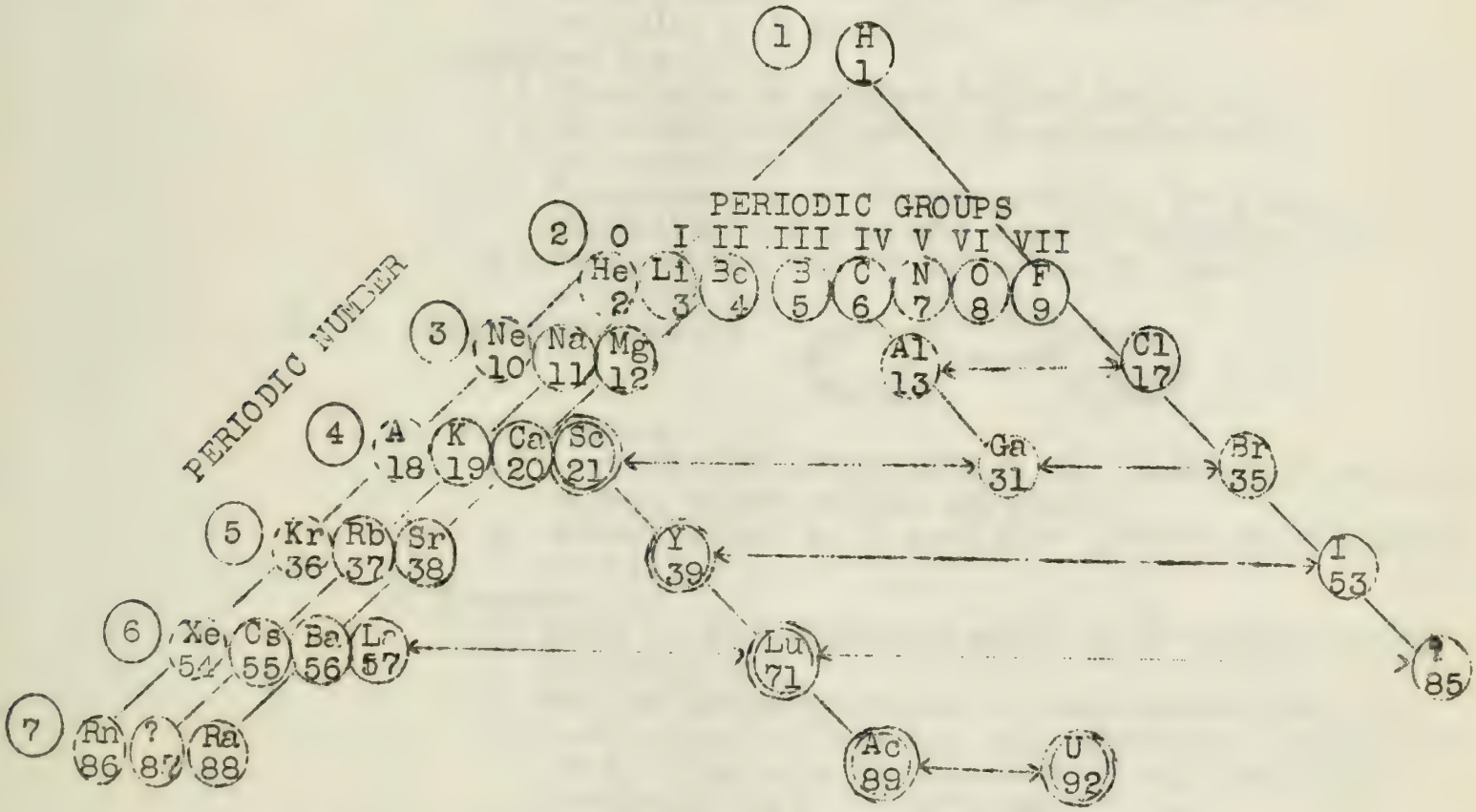
Donald R. Martin

The new table is simply a different geometric configuration of the Bohr table. Hydrogen is made the apex of an isosceles triangle, one side of which is the alkali metal family and the other side the halogen family. Thus the relationship of hydrogen to both families is shown. By such a configuration all the rare earths then fall into their regular position in the 6th series.

The four different types of elements as classified by Bohr are shown by different types of circles around the elements.

The electronic configuration of, Werner's coordination number of, the minimum and maximum valence exhibited by, the elements are also included in the table.

The abbreviated table below shows the general configuration of the table:



Electrons in Quantum Groups

Periods	K	L	M	N	O	P	Q
1	Z						
2	2	Z					
3	2	8	Z				
4	2	8	Y	Z			
5	2	8	18	Y	Z		
6	2	8	18	X	Y	Z	
7	2	8	18	32	X	Y	Z

Types of Elements

All groups Complete	2 Groups Incomplete
1 Group Incomplete	3 Groups Incomplete

Sloping Lines Represent Degrees of Similarity

————————	Very close similarity
——— ———	Close similarity
— — — — —	Some similarity

Wagner, H. A. and Booth, H. S., J. Chem. Ed. 22, 128-9 (1945).

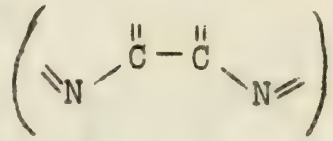
COORDINATION COMPLEXES OF DIPYRIDYL AND RELATED SUBSTANCES

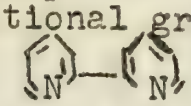
F. W. Cagle

April 3, 1945

I. Coordinating Agents

A. Pyridine (functional group )

B. Compounds with the functional group 

1. 2, 2'-bipyridyl 

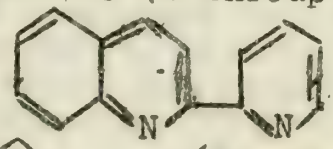
   a. Derivatives
      1) Substitution in the 3, 3' position destroys coordination ability.
      2) Substitution in 6 position reduces coordination ability.
      3) Substitution in 6, 6' position destroys coordination ability.

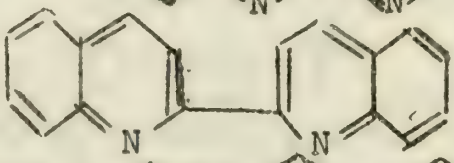
   b. Preparation
      1) Pyrolysis of copper 2-picolinate (1).
      2) Decarboxylation of 3, 3'-dicarboxy-2, 2' bipyridyl (2).
      3) Condensation of 2-brompyridine by ethyl magnesium bromide and cobalt chloride (3).
      4) Dehydrogenation of pyridine by ferric chloride (4).

2. 1, 10-phenanthroline 

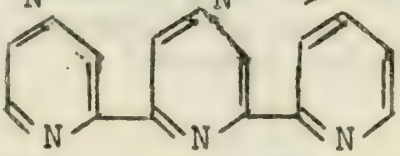
   a. Derivatives
      1) Products of substitution in 5 and/or 6 position retain coordination ability.
      2) Substitution in 3 position lowers coordination ability.

   b. Preparation
      1) From 1, 2-phenylenediamine by a double Skroup reaction (5).
      2) By the transformation of 2-nitroaniline into 8-amino-quinoline and the subsequent formation of 1, 10-phenanthroline (2 Skroup reactions involved) (6).

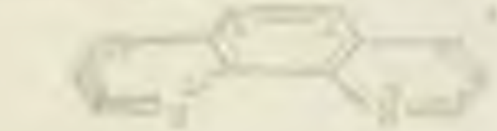
3. 2-(2' pyridyl)-quinoline  (7)

4. 2, 2'-biquinolyl  (7)

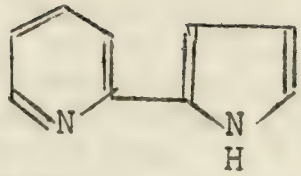
C. Miscellaneous related compounds.

1. 2, 2', 2"-terpyridyl 

   (a byproduct from the preparation of 2, 2'-bipyridyl by dehydrogenation of pyridine)

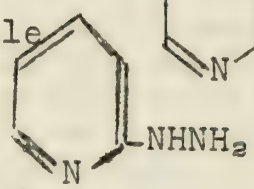


2. 2-(2' pyridyl)-pyrrole



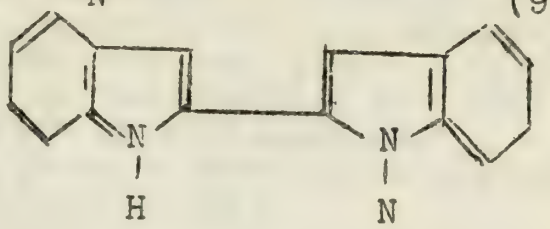
(8)

3. 2-pyridylhydrazine



(9)

4. 2, 2'-bi-indoyl



(10)

II. Complex Compounds

A. Complexes with pyridine involving simple coordinate bonds.

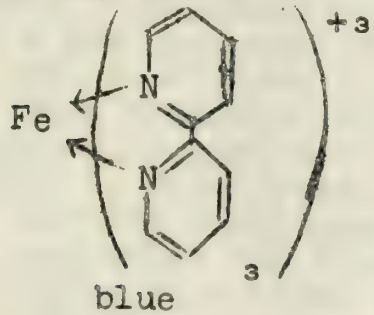
1. Some of these are $[Fe(Py)_4](SCN)_2$, $[Cd(Py)_2(SCN)_2]$, and $[Co(Py)_4](SCN)_2$.
2. Such compounds have been used for the determination of Cu^{+2}(11), Ni^{+2}(12), Cd^{+2}(13), Co^{+2}(14).

B. Pyridine complexes of a chelate nature.

1. Complexes with iron.

a. With 2, 2'-bipyridyl

Ferrous iron forms a bright red complex (15). We may write



$$+ e^- = \underset{\text{red}}{\left[Fe(bipy)_3\right]^{++}}$$

E (formal)(16) = 0.97V

bipy = 2,2'-bipyridyl

This bright red complex is often employed for the colorimetric determination of iron (17).

b. With 1, 10-phenanthroline and its substituted products.

Ferrous iron forms red complexes with these compounds (5). These compounds are used in the qualitative and quantitative determination of iron (18,19), and as oxidation-reduction indicators (20). phen = 1, 10-phenanthroline.

$$\underset{\text{blue}}{\left[Fe(phen)_3\right]^{+3}} + e = \underset{\text{red}}{\left[Fe(phen)_3\right]^{+2}} \qquad E(f) = 1.06 \ (21)$$

For other members we observe similar reactions with the following E (formal) values.

Indicator as $FeSO_4$ Complex	E (formal) volts (21)
5-Nitro-phen	1.25
5-Methyl-6 Nitro-phen	1.23
5-Bromo-phen	1.12
5-Chloro-phen	1.12
5-Methyl-phen	1.02

c. With 2,2',2"-terpyridyl
Ferrous iron gives a reddish purple compound (22). No value for the E(f) can be given. This reagent is superior for small amounts of iron. The ferrous complex has the formula, $[Fe(terpy)_2]^{+2}$.

d. Complex with 2-pyridylhydrazine
Ferrous iron forms a purple complex with this reagent. The structure of this is in question (23,24,25). In any event, the material is never employed to estimate iron since it does not conform with the Beer-Lambert law (25).

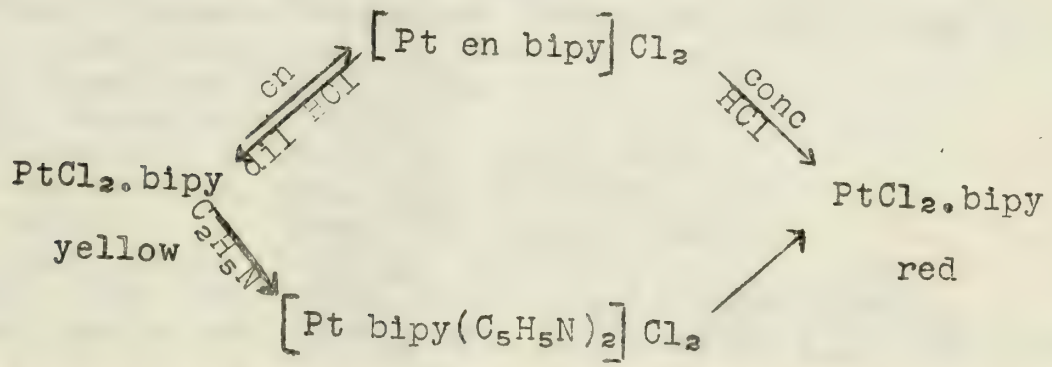
e. Complex with 2-(2' pyridyl)-pyrrole
Ferrous iron gives a reaction completely analogous to that in (d) above (26).

f. With 2-(2' pyridyl)-quinoline
A red color is produced with Fe^{+2} (27). The Fe^{+3} form is not described and the E(f) for the couple is unknown. There is some question concerning the ferrous complex (25).

2. Complexes with ruthenium
a. With 2, 2'-bipyridyl.
A bright red complex of the formula, $[Ru(bipy)_3]\ Cl_2.6H_2O$, may be prepared (28). This results from heating 2, 2'-bipyridyl and $RuCl_2$ together.

b. With 1,10 phenanthroline.
A red compound of presumably the same structure as that given for the dipyridyl analogue has been prepared (29).

3. Complexes with platinum
a. With 2, 2'-bipyridyl.
Several complexes of this type are known but the one which has received the most attention is $PtCl_2$.bipy which exists in anomalous isomers (30,31).



b. Complexes with 2, 2', 2"-terpyridyl.
A situation entirely analogous to that with 2, 2'-bipyridyl is found here (32).

4. Complexes with copper.
a. With 1, 10-phenanthroline
A brown cuprous compound of unknown composition is formed. This has been used for the colorimetric estimation of traces of copper (33, 34).

b. With 2, 2'-biquinolyl
A compound similar to that in (a) above is formed and has been used for the determination of copper (35).

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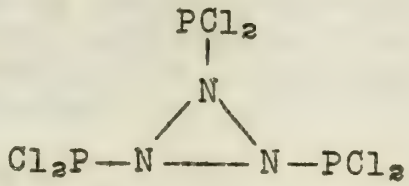
PHOSPHONITRILIC CHLORIDES AND "INORGANIC RUBBER"

L. J. Edwards March 29, 1945

It was shown by Liebig (6) in 1832 that when phosphorus pentachloride is treated with dry ammonia and the product heated, a white stable material is obtained to which Laurent (5) assigned the empirical formula $PNCl_2$. On the basis of vapour density studies Gladstone and Holmes (4) represented the compound as $(PNCl_2)_3$. It has since been realized that the trimer is the lowest member of the series of polymers.

Numerous disagreements have arisen concerning the structure of these polymers and several postulations were made to account for their physical and chemical properties. Because of the stability of these compounds towards heat and hydrolyzing agents, as well as the requirements of valency, cyclic formulae have been assigned to the halonitrides in which the rings are composed either of $>N-PCl_2$ or of $\geqslant N$ and $\geqslant PCl_2$ alternately (11, 12). Wichelhaus suggested the following cyclic formula for the trimer:

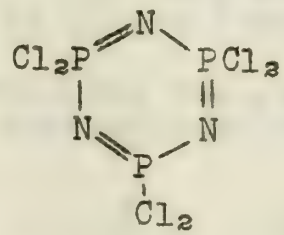


(I)

After an extensive study of the hydrolysis of the trimer, Stokes (11) thoroughly disagreed with this structure, stating that since,

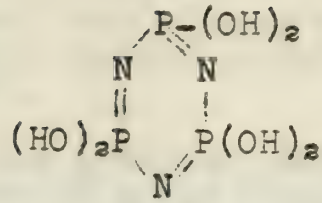
1) the compound decomposes into orthophosphoric acid and ammonia,
2) it is formed from ammonia and phosphorus pentachloride,
3) there are no indications of double or triple linked phosphoric acids or of hydrzine in the decomposition products,

it is probable that the phosphorus atoms are united by nitrogen atoms. Therefore, he agreed with the structure:



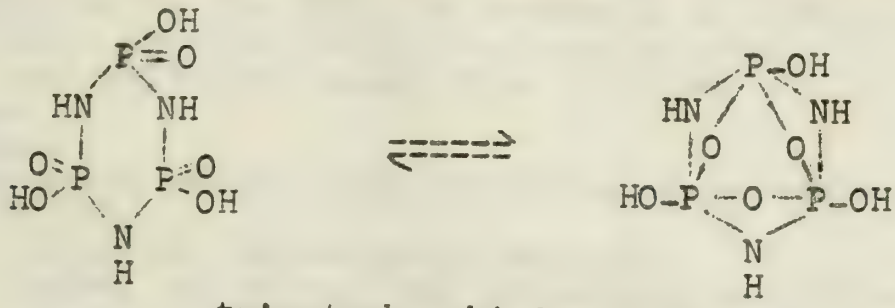
(II)

If this series of phosphonitrilic chlorides is considered to be made up of acid chlorides analogous to $POCl_3$, and if formula II is assumed to be the correct structural representation of the trimer, then hydrolysis should yield triphosphonitrilic acid corresponding to the form:



(III)

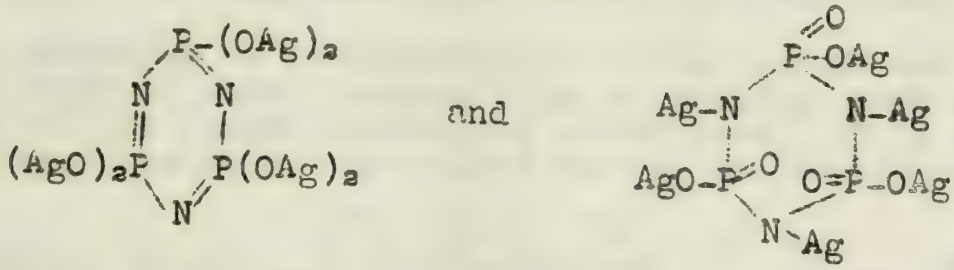
By analogy to many organic compounds, it is not unlikely that this acid could undergo transformation into the tautomeric form:



(IV)

trimetaphosphimic acid

Stokes found that by properly controlling the conditions of reacting sodium trimetaphosphimate with silver nitrate, two crystalline salts could be obtained in fairly pure form. The two compounds correspond to the following:

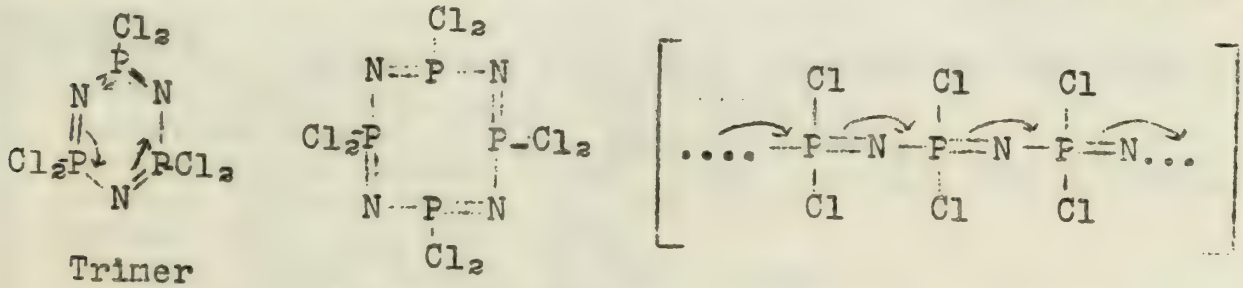


and

(V)

The angle of least strain of the polygons is known to be 135°, which is most closely realized in the tetramer compound, which is the most stable of the series. Both the trimer and tetramer have been subjected to X-ray studies. The data obtained lead to the conclusion that the tetramer is in the form of a puckered ring.

Resonance occurs between the two possible arrangements of the double bonds in the rings analogous to that in aromatic compounds.



Trimer

Tetramer

higher polymers

(VI)

Audrieth and co-workers (1) state that "all the experimental evidence points to the fact that both the trimer and the tetramer possess cyclic structures with alternate phosphorus and nitrogen atoms, whereas the higher members including the 'inorganic rubber' possess chain structures".

An examination of the physical properties of these polymers reveals a distinct change in going from the tetramer to the pentamer. The trimer and tetramer are also less easily polymerized than the higher members which indicates their ring structures.

In addition to the definite compounds of $(PNCl_2)_x$ which have been discussed, the following have been reported: (8, 2, 3)

a. a high molecular weight oil, in which x = 11.
b. gums
c. waxes
d. inorganic rubber, with an extimated molecular weight of 20,000.
e. an infusible, non-elastic material.

Below 250°C. the trimer and tetramer give little or no polymeric material, whereas the oily polyhomologs are converted rapidly to rubbery masses below 200°C. Schenck and Römer (10) describe the polymer as an elastic and pliable material like rubber. In the pure state it is colorless and insoluble in the usual organic solvents. The elastomer is stable towards acids and alkalies but is decomposed by prolonged boiling with water.

The mechanism of polymerization of the trimer and of the tetramer, both of which possess ring structures, must be different from that of the higher chain-like structures. It is supposed that the following reactions take place during polymerization:

$$(PNCl_2)_3 \longrightarrow \ldots \overset{Cl_2}{\overset{|}{P}}-N=\overset{Cl_2}{\overset{|}{P}}-N=\overset{Cl_2}{\overset{|}{P}}-N \ldots \longrightarrow (PNCl_2)_2 + PNCl_2$$

ring rupture

or

$3PNCl_2$

In substantiation of this postulated mechanism, Audrieth and co-workers consider the depolymerization of inorganic rubber, which always gives appreciable quantities of the trimer and tetramer as well as oily and waxlike polyhomologs.

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THE HALIDES OF SILICON

Margaret Kramer April 24, 1945

I. Introduction

The hydrogen atoms in the silicon hydrides may be replaced atom for atom by halogen. As with carbon, chain halogen derivatives may thus be built. Of the elements in Group IV, germanium alone exhibits a similarity to silicon in the formation of certain compounds.

II. Fluorine derivatives.

Only two fluorides of silicon are known, SiF_4, and Si_2F_6.

A. Completely halogenated.

1. Silicon tetrafluoride is prepared from silica or silicon and HF, or from silicon and fluorine.
2. Si_2F_6 is prepared by action of ZnF_2 on Si_2Cl_6 (1).

B. Properties.

Both of the fluorides are colorless gases, readily hydrolyzed by water.

$3SiF_4 + 3H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6$

$2Si_2F_6 + 4H_2O \longrightarrow H_2 + H_2Si_2O_4 + 2H_2SiF_6$

C. Subfluorides have been reported, but have not been established (2).

Halohydrides

A. Preparation

Recently the series SiH_3F, SiH_2F_2, and $SiHF_3$ have been prepared by action of SbF_3 on the corresponding chloride, and subjecting the products to fractional distillation (3).

B. Properties

All undergo slow disproportionation to produce SiF_4 and SiH_4.

$4SiHF_3 \longrightarrow 3SiF_4 + 2H_2 + Si$ (5)

$4SiHF_3 \longrightarrow SiH_4 + 3SiF_4$ (4)

$SiHF_3$ forms an explosive mixture with air.

III. Chlorine derivatives.

This series is more completely known, derivatives from $SiCl_4$ to $Si_{10}Cl_{22}$ having been prepared. Some of the intermediate members are not known, however.

Completely halogenated.

A. Preparation

1. $SiCl_4$ from Cl_2, SiO_2 and C at elevated temperatures; or from ferrosilicon and chlorine. Holding the temperature around 550° results in a 94% yield (6). At lower temperatures some Si_2Cl_6 is produced (7).
2. Higher members are produced from a Ca-Si alloy and chlorine if the temperature is held sufficiently low. A mixture of the following composition is thus produced:

65% $SiCl_4$
30% Si_2Cl_6
4% Si_3Cl_8
1% { Si_4Cl_{10}, Si_5Cl_{12}, Si_6Cl_{14} } separated by fractional distillation (8).

Metallic chlorides have been used as chlorinating agents; e.g., $CuCl_2$, $PbCl_2$ (2). Schwarz and coworkers have prepared $Si_{10}Cl_{22}$ by action of $SiCl_4$ and its decomposition products with hydrogen at high temperatures (9,10,11). The following mechanism was suggested to account for the formation:

$SiCl_4 \xrightarrow{-Cl} SiCl_3 \xrightarrow{SiCl_3} Si_2Cl_6 \xrightarrow{-Cl} Si_2Cl_5 \xrightarrow{SiCl_3} Si_3Cl_8$, etc.... $Si_{10}Cl_{22}$. $SiCl_4$, Si_2Cl_6, Si_3Cl_8, $Si_{10}Cl_{22}$ were identified in the reaction products.

B. Properties

Lower members are colorless liquids. Si_6Cl_{14} and up are white solids. They hydrolyze readily, and fume in moist air. Vapors of the higher chlorides flame in air.

Increasing the temperature during the preparation of the chlorosilicons generally leads to increasing amounts of silicon tetrachloride. This fact has led to the suggestion that upon chlorination, complex silicons are first built up containing the Si-Si links originally in the element. Further chlorination plus heat cause these linkages to be broken, the final product being $SiCl_4$ (7).

An alternate view is that silicon tetrachloride is first formed which by reaction with Si produces Si_2Cl_6 etc. One objection to this is that ferrosilicon when heated with silicon tetrachloride, does not produce higher derivatives (5).

Hydrolysis of the chlorides may proceed stepwise:

$$SiCl_4 \xrightarrow{H_2O} SiCl_3(OH) \xrightarrow{H_2O} SiCl_2(OH)_2 \xrightarrow{H_2O} SiCl(OH)_3$$

$$\xrightarrow{H_2O} Si(OH)_4$$

This may be controlled by diluting the compound with anhydrous ether and using a moist organic solvent for the hydrolysis (2).

$SiCl_4$ also reacts with $(Me_4N)_2SO_3$ in liquid sulfur dioxide, precipitating SiO_2xSO_2 (12). This dissolves in excess reagent at low temperatures, but reprecipitates upon warming to 0°.

With ammonia, under temperature control, silicon tetrachloride forms a series of compounds, including $Si(NH_2)_4$, $HNSi(NH_2)_2$ ... Si_3N_4 (13).

C. Subchlorides

$(SiCl_2)_x$ has been prepared by passing $SiCl_4$ and H_2 over a glow discharge (14). $(SiCl)x$ has been prepared by cracking $Si_{10}Cl_{20}H_2$ or $Si_{10}Cl_{22}$ at 300° (10).

Halohydrides

A. Preparation

These are prepared by action of HCl on SiH_4 in the presence of $AlCl_3$. Direct reaction with halogen is explosive and must be carried on at low temperatures. $CHCl_3$ may also be used to produce higher chlorosilanes.

B. Properties -- these too hydrolyze readily and react with ammonia (15).

IV. Bromine derivatives.

The bromine derivatives both in preparation and properties resemble the chloro compounds. This series is not as completely known, however, having been prepared only as far as Si_4Br_{10}. $SiBr_4$ is a liquid, the succeeding members are crystalline solids.

Silicobromoform is spontaneously inflammable when poured through air. It hydrolyzes readily and rapidly.

V. Iodine derivatives

These are less stable than the chloro or bromo derivatives.

A. Preparation

1. SiI_4 from silicon and iodine in an atmosphere of carbon dioxide.
2. Si_2I_6 from: $SiI_4 + 2Ag \xrightarrow{300^\circ} Si_2I_6 + 2AgI$

Heating decomposes this into SiI_4 and $(SiI)_4$ (16).

Iodosilanes have been prepared from SiH_4 and HI (17). The iodosilanes are liquids with pungent odors, decomposing in sunlight. $SiHI_3$ forms an explosive mixture with air. The iodosilanes also hydrolyze readily.

VI. Mixed halides

Mixed halides containing 2 different halogens and 3 different halogens are known (18,19,20,21). Halides of the type SiWXYZ or SiHXYZ are not yet known.

The general methods for their preparation are:

$$SiCl_4 \xrightarrow[SbF_5]{SbF_3} SiF_2Cl_2 . SiF_3Cl$$

These are gases, hydrolyzable to hydrated silica, fluosilicic acid, and HCl. They have nauseating odors and are irritating to inhale (18).

$$Si_2F_6 + XsBr_2 \longrightarrow SiF_2Br_2 + SiF_3Br + SiF_4$$

These two are colorless gases, readily hydrolyzed by moist air (19).

Complete series of chlorobromides, chloroiodides, and bromoiodides are known.

More recently derivatives containing 3 halogens have been prepared (20).

$$4SiFBr_3 + 3Cl_2 \longrightarrow 2SiFClBr_2 + 2SiFCl_2Br + 3Br_2$$

$$SiFBr_3 \xrightarrow{SbCl_3} SiFCl_2Br + SiFClBr_2$$

$SiFCl_2Br$ and $SiFClBr_2$ hydrolyze with ice cold water to silicic, hydrochloric, hydrobromic, and fluosilicic acids.

VII. Oxyhalides

Oxyhalides of fluorine, chlorine, and bromine are known (2,22,23).

A. Preparation

A fluoro derivative is prepared by action of SbF_3 on Si_2OCl_6.

The chloro and bromo oxyhalides are prearred by action of bromine or chlorine and oxygen on silicon at high temperatures:

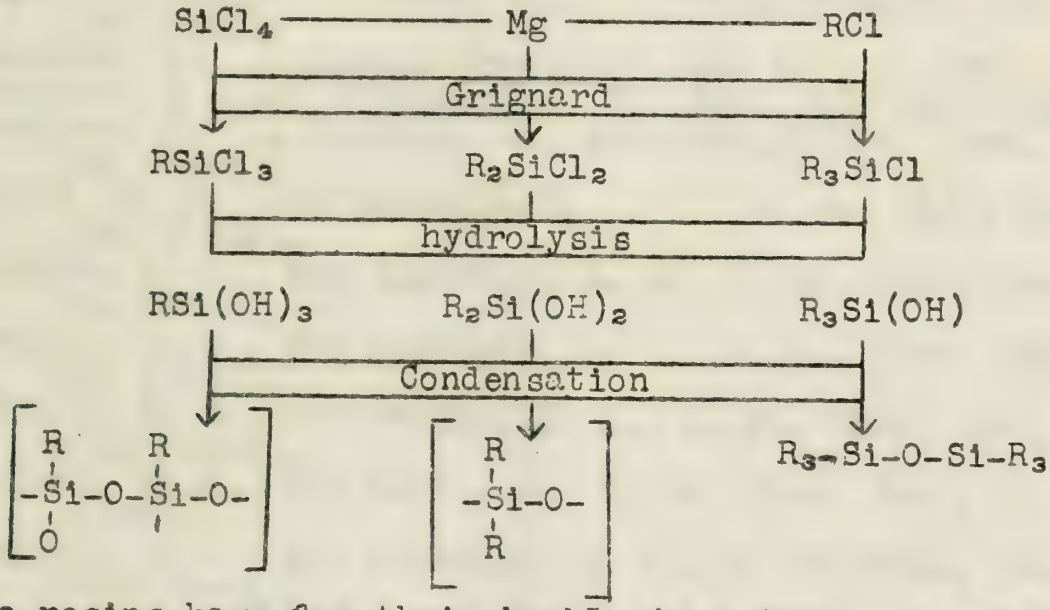
$$Si + O_2 + Br_2 \xrightarrow{700^\circ} (SiOBr_2)_4 + Si_2OBr_6 + Si_3O_2Br_8 + Si_4O_3Br_{10} + Si_5O_4Br_{12}$$

B. Properties

The oxyhalides are colorless, oily liquids, except for $(SiOCl_2)_4$ and $(SiOBr_2)_4$, which are solids. They hydrolyze readily. They react with absolute alcohol to form ethyl esters. The esters are colorless, oily liquids with high boiling points, which hydrolyze slowly, even at 100°.

VIII. Silicon plastics.

Recently the silicones have been shown to be of commercial importance. Since their preparation depends upon the properties of the silicon halides mentioned above, they are included briefly here.



(24, 25)

The resins have for their backbones a framework of Si atoms joined by O to each other -Si-O-Si-. The resins are much more stable thermally than the best of organic resins (26). They show relatively little change of viscosity over quite a temperature range.

The resins actually stem from the work of Kipping in England (27) who in 1937 had said that the outlook for this branch of silicon chemistry was not very hopeful.

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ROLL CALL

April 17, 1945

Synthetic Optical Crystals

A. L. Oppegard

Synthetic optical crystals of sodium chloride, potassium bromide, lithium fluoride and sodium nitrate are being made by the Harshaw Chemical Company. The crystals are 8" in diameter, 10 1/2" high, and weigh about 35 pounds. A 60° lithium fluoride prism with a 19mm. face and 15mm. high costs $1000.

The crystals are made of pure salts in platinum crucibles. The crucibles have a cone shaped bottom, weigh 850 grams and cost $900. One crucible can be used to make twenty sodium chloride crystals but can be used to make only four lithium fluoride crystals.

The platinum crucible containing the molten salt is placed in a special oven. The oven is a vertical cylinder divided into a lower and upper oven. The crucible is placed in the upper oven and is gradually lowered by a snychronous motor to the lower oven. It takes about a year to determine the optimum conditions with respect to temperature gradient and rate of lowering.

When the temperatures in the ovens are right, the lowering mechanism is started, and a cold pin placed against the tip of the cone shaped bottom to start crystallization. It is thought that the cold pin starts many microscopic crystals, and then one forges ahead to form the main crystal. The growth of the crystal takes 7-10 days, and there is no way of telling beforehand whether one crystal or several have formed.

The crystal is removed from the crucible much as an ice cube is removed from an ice tray, i.e., intense heat is applied to the outside of the inverted crucible. After annealing for 7-10 days, the crystal is ready to be split or sawed into the desired shape.

The value of these crystals lies in the fact that they are much larger than natural crystals and permit the manufacture of large prisms and other optical equipment for infra red spectographs. By the use of the infra red analysis petroleum fractions can be identified in five minutes where it used to take days by other means.

Reference

Taylor and Kremers, Chem. Ind., LV, No. 7, page 906 (1944).

[illegible]

April 27, 1961

[illegible] Optical Crystals

A. L. [illegible]

[illegible] optical crystals of medium density, potassium iodide, lithium fluoride and sodium nitrate are being grown by the Harvard Chemical Laboratory. The crystals are 8" in diameter, 10 1/2" long, and weigh about 20 pounds. A 60° lithium fluoride prism with a 12mm. face and 12mm. right angle.

The crystals are made of pure salts in platinum crucibles. The crucible rests on a cone shaped support, which has a small hole. The crucible is set into the hot zone of a vertical tubular furnace. The crucible is made to move slowly upward. The crystal is then in a state to make only very little [illegible] crystals.

The platinum crucible containing the molten salt is placed in a special oven. The oven is a vertical cylinder divided into a lower and upper oven. The crucible is placed in the upper oven and is gradually lowered by a mechanism outside to the lower oven. It takes about 8 hours to lower the crucible. [illegible] will result in inconsistent product and risk of invisible.

When the temperature in the lower oven rises, the lowering mechanism is started, and a motor and chained spindle the rise of the cone shaped support to assist crystallization. It is thought that the cone gives more uniformity. It is thought [illegible] allowed to turn the main crystal. The growth of the crystal takes 7-12 days, and there is no way of seeing information [illegible] for crystal at present [illegible].

The original is recovered from the crucible with as an [illegible] is removed from an [illegible] lithium [illegible] is [illegible] of the [illegible]. After annealing for 7-10 days, the crystal is ready [illegible] and [illegible] [illegible].

The value of these crystals lies in the fact that they are larger than [illegible] and permit the manufacture of large prisms and other optical equipment for infrared spectrophotometers. By the use of [illegible] and [illegible] [illegible] can be identified by [illegible] [illegible] [illegible] [illegible] by [illegible].

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[illegible] Chem. Eng., [illegible], 37, No. 7, [illegible] (1961).

ROLL CALL

Solvent Effect of Lithium Nitrate on Zinc Acetate in Acetic Acid

Nancy Downs

Zinc acetate is only slightly soluble in acetic acid. Upon the addition of sodium or ammonium acetate the solubility of zinc acetate increases. Special chemical effects may enter into the solvent action of acetates. The authors believe that the salt effects may be large for acetic acid because of the low dielectric constant of acetic acid.

The effect of a neutral salt, lithium nitrate, on the solubility of zinc acetate was studied.

Several methods of procedure were applied. One involved the freezing points of solutions containing fixed amounts of lithium nitrate and variable amounts of zinc acetate. The solubility was obtained over the range from 40°-80°. The other method was to prepare solutions of known proportions of lithium nitrate and acetic acid, and to add excess zinc acetate. After sealing these mixtures in tubes and keeping the tubes at constant temperature for several weeks, the samples were removed and analyzed.

The results showed that lithium nitrate increases the solubility of zinc acetate but not to the same extent as the sodium acetate or ammonium acetate.

The large difference in the solubility of the zinc acetate in acetic acid containing lithium nitrate and containing sodium acetate is explained by chemical interaction in the behavior of zinc acetate to other acetates.

Reference: Griswold, Ash, and McReyholds, J. Am. Chem. Soc. 67, 3, 372 (1945).

Comparison of the Ammines of Cobalt and Copper

J. V. Quagliano

The bonding power of the $Cu-NH_3$ bond in $Cu(NH_3)_4^{++}$ is much weaker than the $Co-NH_3$ bond in $Co(NH_3)_6^{+++}$. In aqueous solution the cobalt complex is more stable, that is, much ammonia is liberated when the hexammine cupric salt is dissolved in water. As regards the bonding power and the stability of the ions, consider the electronic configurations:

	3d					4s	4p		
Cu^{++}	xx	xx	xx	xx	x				
$Cu(NH_3)_4^{++}$	xx	xx	xx	xx	..|	..|	..	..	x

The one unpaired electron in the 3d orbital "jumps" to the 4p level (these orbitals have about the same energy). The stability depends mainly on s- and p- orbitals and the configuration of the complex ion is planar.

In the case of cobalt, we have:

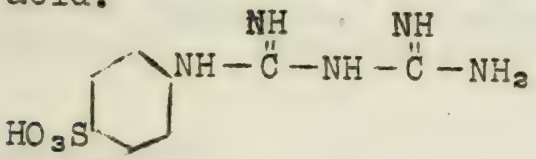
	3d			4s	4p		
Co^{+++}	xx	xx	xx				
$Co(NH_3)_6^{+++}$	xx	xx	xx	.. ..	..	.. ..	..

In the hexammine cobaltic ion, two d orbitals are available for combination along with s and p and these six orbitals have their bonds directed toward the corners of a regular octahedron. The cobalt complexes, as is general of the complexes of the transition elements, differ from those of copper. The size and charge of the cations are not sufficient to explain the chemistry of an element, for one must also consider the covalent energy involved.

Complex Compounds of Phenylbiguanide-p-Sulfonic Acid

Margaret Kramer

Continuing a series of investigations on complexes formed by biguanide and its substitution products with Ni^{++}, Cu^{++}, Co^{+++}, Pd^{++}, and Cr^{+++}, Ray has recently reported the preparation of complexes of Co^{+++}, Ni^{++} and Cu^{++} with phenylbiguanide-p-sulfonic acid:



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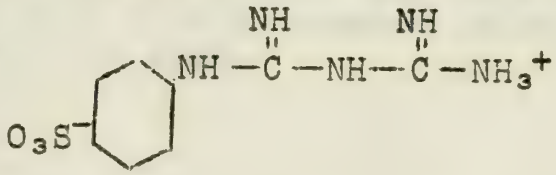
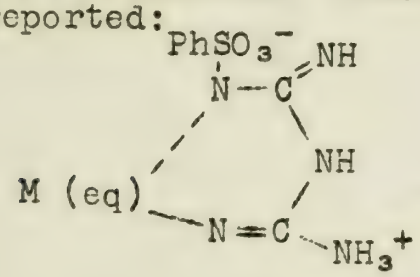


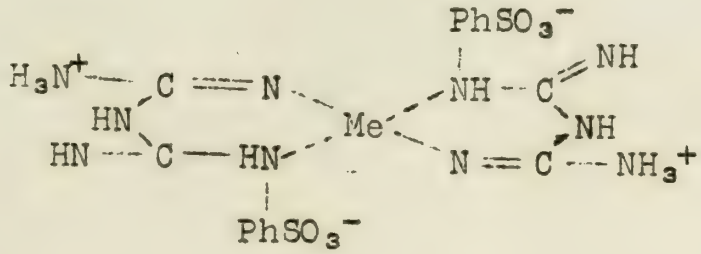
II "Zwitter ion"

The substance is practically insoluble in water due to internal salt formation. Insoluble complexes of the following type are reported:



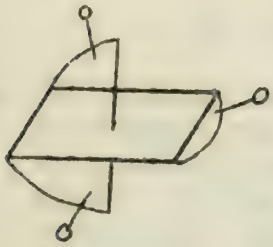
M (eq) = 1/2 Cu^{++}, 1/2 Ni^{++} or 1/3 Co^{+++}

The four-coordinated complexes of copper and nickel are planar, and show cis- trans isomerism. Only 1 form was isolated, probably the trans form, since the cis form should be relatively unsoluble because of the proximity of two negative groups:



trans

The cobalt complex (octahedral) ought to show geometric isomerism:



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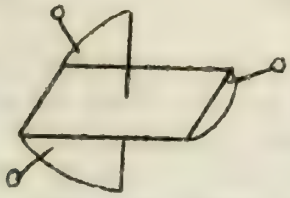
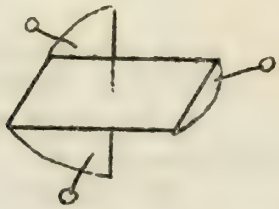


II



III

ρ = $PhSO_3^-$

III should be most stable because of the distance of the $PhSO_3^-$ groups from each other.

Coordination with copper or nickel increases the acid character of the ampholyte. Coordination with cobalt somewhat enhances the strength of cationic acid and anionic base.

Reference:

Ray, P. and Siddhanta, S., J. Ind. Chem. Soc. 20, 250 (1943).

THE DETERMINATION OF CRYSTAL STRUCTURE

K. J. Pipenberg May 1, 1945

I. Introduction. The crystalline state has long intrigued investigators. The methods and tools of research were limited to optical methods in the visible range--which permitted a study of the outer form only. With the discovery by Friedrick, Knipping, and Laue (1) that x-rays could be diffracted by crystals which acted as three-dimensional gratings, a new door was opened--that of complete analysis of the crystalline state.

II. Methods Used. Many techniques of recording x-ray diffraction patterns have been devised; of these, four have found wide use (2-8).

A. Powder Method (2-7). An essentially monochromatic beam is permitted to impinge on a finely powdered sample. The crystal fragments of the sample are randomly orientated so that smooth concentric rings or arcs are recorded on the cylindrical film. The pattern recorded on the film is a "fingerprint" of the compound.

B. Laue Method (2-7). A single fixed crystal is placed in the path of an x-ray beam containing all wave lengths. A pattern of symmetrical spots is recorded on a flat film. Each plane in the fixed crystal selects a wave length from the x-ray beam so that the Bragg Law, $n\lambda = 2d\sin\theta$, is satisfied.

C. Rotation or Oscillation Method (2-8). A single crystal is rotated or oscillated about one of its axes in a monochromatic x-ray beam. The pattern, which consists of a series of spots lying on parallel lines, is registered on a cylindrical film, each set of planes recording only when it is in such a position that the Bragg law is obeyed.

D. Weissenberg Methods (2-8). This is a modification of the rotation technique. A single crystal is rotated about one of the principal axes while at the same time the cylindrical film is translated parallel to the axis of rotation. A shield is used so that only one layer line can be recorded at one time. The pattern obtained is a beautiful network of symmetrical spots.

III. General Procedure (4, 5, 6). There is no completely standardized procedure for the determination of a structure. Each new structure becomes a novel problem presenting fresh and unexpected difficulties. The following steps are usually encountered in one form or another.

A. A study of the external symmetry of the crystal--including such physical properties as optical, electrical, magnetic, etc.

B. The determination of the size of the unit cell.
   1. Rotation or oscillation patterns about the principal axes.
   2. Indexed powder patterns.
   3. Laue patterns -- a rough approximation.

C. The determination of the space lattice or scheme of repetition.

D. The calculation of the number of molecules per unit cell.

$$n = \frac{D\ V\ 6.03 \times 10^{-1}}{M}$$

n = number of molecules per unit cell.
D = density.
V = volume in cubic angstroms.
M = molecular weight.

E. The selection of the space group.

F. The tabulation of all possible atomic arrangements.

G. The choice of the correct arrangement.

H. The determination of the parameters of this arrangement that fix the exact position of the atoms in the unit cell.
   1. Deduction method--applicable only to the simplest structures.
   2. Fourier series method.

$$\rho(uvw) = \frac{1}{V} \sum_{h=\infty}^{+\infty} \sum_{k=\infty}^{+\infty} \sum_{l=\infty}^{+\infty} F(hkl) \cos 2\pi(hu + kv + lw)$$

   3. Pattern-Harker Series.

$$P(uvw) = \sum_{h=\infty}^{+\infty} \sum_{k=\infty}^{+\infty} \sum_{l=\infty}^{+\infty} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

   4. Bragg's optical synthesis of Fourier Series.
   5. Huggins' modification of the Bragg method.

IV. An Example. The crystal structure of copper sulfate pentahydrate as determined by Beevers and Lipson (9) illustrates the problems encountered and the methods employed for their solution.

A. Available data which was useful.
   1. Decomposition on heating proceeds in three stages.
      $CuSO_4.5H_2O \rightarrow CuSO_4.3H_2O \rightarrow CuSO_4.H_2O \rightarrow CuSO_4$
   2. Four waters are replaceable by ammonias, while the fifth is not.
   3. Jordahl (10) predicted from magnetic susceptibilities the ~~tetra~~octahedral arrangement of oxygens around the copper atoms.
   4. Optical examination (11) indicated a tricilinic system, with centro symmetry.
      a. Space Group -- C_1^1
      b. Axial ratio: a:b:c = 0.5715:1:0.5575.
      c. Angles: $\alpha = 82°16'$, $\beta = 107°.26'$, $\gamma = 102°40'$.
      d. Well developed [001] zone.

B. X-ray Data.

1. From oxcillation patterns the unit cell dimensions were found to be

$$a_o = 6.12 \text{ Å}$$
$$b_o = 10.7 \text{ Å}$$
$$c_o = 5.97 \text{ Å}$$

The volume of the crystal was calculated to be 363 Å^3.

2. The number of $CuSO_4.5H_2O$ per unit cell calculated to be 2.
3. From the extinctions noted on the photographs, the space group was found to be C_i^1 -$P\bar{1}$.
4. Determination of copper and sulfur positions.
5. The complications which arose in the establishment of the other atomic positions prevented the direct solution of the structure. The intensities of 89 (hk0) reflections were measured (12) and the Fourier projection (13) of the unit cell on the (001) plane was made, establishing the remaining positions.
6. The structure obtained was verified by a comparison of the observed and calculated (14) intensities.

C. Discussion of the structure. The copper atoms lie on the special positions (000) and ($\frac{1}{2}\frac{1}{2}$0) and the sulfur upon the general position (0.01 0.29 0.64). Four waters are arranged in squares around the coppers, and two oxygens with these form an approximate octahedron. The fifth water is not coordinated, but is in contact with two oxygens and two waters.

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5. P-wave data.

6. Plus validation datasets using both soil and structures were found to be

$$R_1 = 0.02 \ \%$$
$$R_2 = 10.7 \ \%$$
$$R_3 = 0.0 \ \%$$

The values of the dynamic was indicated to be 0.7 %.

8. The number of the "soil" was only medium-low to be 2.

9. Since the earthquake occurred at the centroid, the epicenter error was found to be 0.1 mi.

4. Determination of proper and minor periods.

5. The correlations which exist in the material-soil of the other actual buildings greatly the stress pattern of the structure. The properties of (100) particles were measured (12) and the properties (120) of the soil as in the (100) place may vary, substituting the regularly particles.

6. The effective dynamic was applied to a composite of the phenomena and also taken (1), intensities.

7. Intensity of the structure. The upper floor (1) of special positions (100) and (120) and the entire upper floor position (0,0; 0,20; 0,40). Four metres are measured in square around the square, and the corners with those from an accelerometer arrangement. The first water is not conditions, but is in direct with the response and the weather.

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SIR HUMPHRY DAVY

Virginia Bartow May 8, 1945

I. Youth and Education -- 1778-1798.
  1. Born -- Penzance, Cornwall, December 17, 1778.
  2. Ancestors among the 200 year old families of Cornwall.
    a. Grandfather a builder.
    b. Father a woodcarver and farmer, Died in 1794.
    c. Mother a milliner.
  3. Education
    a. Mr. Bushnell -- for reading and writing.
    b. Grammar school from six to fourteen.
    c. Truro -- The Reverend Mr. Coryton one year 1793.
    d. 1794, a year unsettled, no responsibility.
    e. 1795, Elaborate scheme of self study comprising all the Liberal Arts.
    f. 1795, Apprenticed to Dr. Borlase -- surgeon and apothecary of Penzance.
      1. Influential studies -- Mathematics, Nicholson's "Dictionary of Chemistry" and Lavoisier's "Elementary Chemistry"; Locke, Berkeley, Hume, Condorcet and Kant.
      2. Friends Gregory Watt and Davies Gilbert
      3. Essays on Heat and Light.

II. Establishment of Reputation, 1798-1812.
  1798 1. Pneumatic Institute at Clifton near Bristol under Dr. Beddoes.
  1801 Royal Philosophical Institution --
    Assistant -- Lecturer in Chemistry and Experimenter.
    Professor of Chemistry
    Establishment of Popular Lectures
    Research both of his own choosing and that of his directors.
  1812 Knighted.
    Marriage to Mrs. Aprecee -- incompatibility of temperament.
    Resignation from the lectureship at the Royal Institution.
    L.L.D. and lectures at Dublin.
    Published the "Elements of Chemical Philosophy".
    Retained connections with the Institute.

III. Last Years.
  1813-1815 European Travels -- France, Switzerland, Italy, Austria.
    Faraday, the assistant.
    Corresponding Member of the French Institute.
    Napoleon Prize of the French Institute.
  1818-1820 European Travels.
  1820 Return to England -- Presidency of the Royal Society
  1824 North Sea Voyage -- Sweden, Denmark, Holstein, Hanover.

SIX-MONTHS DAY

Virginia Beach Mo. 6, 1940

I. Study and Education — 1938-1939.
  1. Work — Teacher, Cornell, January 17, 1938.
  2. Lectures during the 3rd year of College of Cornell.
    a. Specifications a bullet.
    b. Father a volunteer-at Center, Dec 31 1938.
    c. Mother a milliner.
  3. Education.
    a. Dr. Cassell — Corrections and writing.
    b. Grammar School from 4th to Junior.
    c. Trips — The Revival in Corpus one year 1937.
    d. 1938, a year unsettled, in readjustment.
    e. 1938, Elaborate scheme of self study correlating (?) the (illegible) acts.
    f. 1938, Convalesced in St. Petersburg — weighed and physicians of Delaware.
    g. Spiritual crisis — Indecision, discouraged, "Dictionary of Geography" not Lexington a "life-saving Christian", Lodge, Berkeley, Tenn. Conformed and Fact.
    h. Florida Library Work and Dailey Oldham
    i. Energy in Fact not Light.

II. Establishment of Department, 1939-1940.
  1939 a. Demonstrate Initiative in Letter Over Retired Labor Dr. Bedford.
  1939 Dogal Philosophical Foundation —
    Assistant — Lecturer in Chemistry and Superintendent.
    Professor of Chemistry
    Establishment of Popular Lectures
    Research work of his (illegible) and that of his Directors.
  1939 Friends.
    Marriage to Mrs. Arrowood — Incompatibility of Temperament.
    Resignation from the Superintendent of the Dogal Institution.
    L.L.D. and Lectures at Salem.
    Published the "Chemistry of Elemental Philosophy".
    Material Association with the Institute.

III. Last Work.
  1939- Diversion Travels — France, Germany, Italy, Austria
  1940 Switzerland, the Netherlands.
    Corresponding Member of the Fraser Institute.
    Business Crisis of the Fraser Institute.
  1940-
  1940 European Travels.
  1940 Return to England — Availability of his Grand Guests
  1940 Earth the Future — Spoken, Lecture, Quizzes, Doctors.

1827 Winter in Italy due to ill health.
1828 Last continental trip for health.
Died at Geneva May 29, 1828.

IV. Estimation of Character.
A poet -- imagination.
A humanitarian -- safety-lamp.
Disposition -- spoiled by success and jealous of rivals.
tactless and irritable toward critics.
unfriendly to Faraday and Davy.
A genuine scientist -- Facility to modify prevalent belief.
Foresaw change of opinion.
Convictions based only upon proof.
Davy's place in history not due to human fraility, incidents of his life or popular audiences. His significance is scientific and the summary of his work is a review of the science of his time and its progress.

V. Scientific Interests and Achievements.
1. Essays on Heat and Light -- youthful speculation.
a. Contemporary theory of combustion -- phlogiston versus oxygen. Temporary substitution of phosoxygen -- a combination of oxygen and light.
b. Heat of Combustion -- ejection of caloric, an imponderable fluid.
-- motion or vibrations of particles.
c. Heat capacity -- products of combustion have less capacity than original substances.
2. Physiological effects of gaseous medication -- N_2O
Contingent research -- composition of HNO_3, NO, N_2O_4 and NH_3.
3. Electrochemical studies.
Consideration of the production of hydrogen and oxygen by the electrolysis of water.
Theory-Ritter, elements at electrodes had been combined with electricity.
-Davy, a conducting chain.
Unexplainable appearance of acid and alkali at electrodes.
Contemporary definitions.
Acid -- the present oxide of a non-metal.
Oxide - A substance not sufficiently oxygenated into an acid.
Salt -- combination of an acid and oxide. (Metal part of oxide and non-metal in acid might not be known).
Trials to eliminate the acid and alkali lead to the discovery of Na, K and later, at an amalgamated electrode, Ca, Ba, Sr and Mg.
Connection established between chemical and electrical affinity.

4. Alkaline nature of K, Na and NH_3.
   K and Na do not contain hydrogen nor does NH_3 contain oxygen. (Subjected to experimental proof).
5. Study of halogens.
   a. Elementary nature of chlorine established.
      Basis -- Chemical properties.
         the "proportions" with which it combines.
         (Mr. Dalton's ingenious idea).
         Dry Cl_2 and Fe in red hot tube } -- same product
         Fe and HCl } -- without water
      Contingent discoveries -- $COCl_2$ and ClO_2--euchlorine.
         HCl, HI and HCN acids have no oxygen.
      Broadens definition of combustion.
   b. Characterized F_2 -- suspected "fluate of calcium".
   c. Solved French riddle by classifying I_2.
6. Composition of the air -- mild combinations.
   Individual gases stirred by an atmospheric turbulence.
   1833, Grahams Law -- gaseous diffusion explained later by the kinetic theory.
7. Chemistry of the diamond.
   Argument for differently arranged particles in apparently elementary forms of matter.
8. Minor experiments.
   Theory of volcanoes.
   H_2Te and PH_3
   Torpedo fish.
   Attempt to get chemical effects from magnetic effects.
9. Practical and humanitarian work.
   Safety lamp -- copper for ships sheathing -- Zinc to preserve boilers.
10. Lectures: Tanning and Agricultural Chemistry.
11. Chemical Philosophy and Predictions.
   1. Appreciation of theories, analogies and hypotheses.
   2. No formulas and no equations.
   3. Elements of bodies merely points possessing weight and attractive and repulsive forces.
   4. Intimate connection between chemical and electrical phenomena.
   5. "One good experiment is of more value than the ingenuity of a brain like Newton's."
   6. Dalton's atoms became "proportions" -- the hypothetical discarded for the practical.
   7. Natural orders of resemblance, K, Na, NH_4 (Gay-Lussac S and O_2) Cl_2, I_2 and O_2.
   8. H_2O as a formula for water -- based on volumes.
   9. Prout's Hypothesis.
   10. Liquifaction of gases by self compression from slow generation. HCl by Davy followed by Cl_2 by Faraday.
   11. All acids contain hydrogen.
12. Conclusion --Davy's greatest success in the realm of facts. His attempts at theory not happy.

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THE HALOGENOIDS OR "PSEUDO-HALOGENS"

Nancy Downs May 22, 1945

I. Definition. "Any univalent chemical aggregation composed of two or more electronegative atoms, which shows in free state certain characteristics of the free halogens, and which combine with hydrogen to form an acid and with silver to form a salt insoluble in water" (1,2).

II. History.

Gay Lussac first isolated cyanogen $(CN)_2$ in 1815 by heating mercuric or argentous cyanide. This was the first isolation of a "radical" as defined by Liebig (3). Liebig tried to isolate thiocyanogen by passing chlorine over silver or lead thiocyanate but he was unsuccessful. Linneman also tried to prepare thiocyanogen but succeeded instead in preparing the interhalogenoid, cyanogen sulfide ($(CN)_2S$) in 1861.

Schneider and Klason also attempted to isolate free thiocyanogen, but in 1901 Goldberg stated that free thiocyanogen had not yet been prepared.

Sommer isolated azido-carbon disulfide $(SCSN_3)_2$ but he did not recognize its true nature. In 1920 thiocyanogen was obtained by Soderback (4). With Soderback's work, new interest arose in the study of "inorganic radicals" and recently many investigations of the halogenoids--their structures, properties and compounds--have been made.

III. The Halogenoids.

A. General properties.

1. Activity or electromotive series (from a study of electrical conductivity measurements) F^-, ONC^-, OCN^-, Cl^-, N_3^-, Br^-, CN^-, SCN^-, $SCSN_3^-$, I^-, $SeCN^-$, $TeCN^-$ (1).
2. Similarities to true halogens.
   a. Halogenoids, in general, are quite volatile.
   b. Solid substances are apparently isomorphous.
   c. In general, they show an affinity for metals, combining directly to form salts. Silver, lead and mercurous salts are insoluble in water.
   d. In general, they form hydracids with hydrogen which in water solution are highly ionized.
   e. They are capable of forming interhalogenoid compounds such as $CN \cdot SCN$, CNN_3, etc.
   f. They form polyhalogenoid complexes such as $Cs(SeCN)_3$, $K(SeCN)I_2$, etc.
   g. Free halogenoids may be prepared, in general, (1) by chemical or electro-chemical oxidation of the hydracids or their salts or (2) by decomposition of the perhalides.

B. Possible explanation of halogenoid properties.

1. Kellermann and Birckenbach use the octet theory (1,5,6).
2. The sum of the valence electrons of the atoms in the halogenoid group can be arranged in saturated shells of eight electrons and an additional shell of seven electrons, similar to that of the halogen atoms.

3. Examples: azide (8 + 7 = 15), selenocyanate (8 + 7 = 15), azidodithiocarbonate (8 + 8 + 8 + 7 = 31).
4. Other radicals also have a total of valence electrons which can be arranged in shells of eight electrons. Ex. NO_3^- (23 = 2 x 8 + 7); OH^- (7).
5. Formula.

Σouter electrons + Σvalence e^- = 8n + 2m - 1.

m = number of hydrogen atoms.

n = number of atoms surrounded by octets.

IV. Thiocyanogen $(SCN)_2$.

A. Preparation.

1. The preparation of thiocyanogen suggested by Inorganic Syntheses is by the oxidation of lead thiocyanate by bromine.

$$Pb(SCN)_2 + Br_2 \longrightarrow (SCN)_2 + PbBr_2 \quad (8).$$

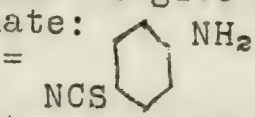
2. Solutions of thiocyanogen may be prepared by oxidation of the free acid by manganese dioxide.

$$4HSCN + MnO_2 = 2H_2O + Mn(SCN)_2 + (SCN)_2$$
$$4HCl + MnO_2 = 2H_2O + MnCl_2 + Cl_2$$

3. Thiocyanogen may also be prepared by electrolysis of thiocyanates, in alcoholic solution (16).

B. Properties

1. Physical.
   a. The solid is a crystalline material which melts at -2 to -3°C.
   b. Liquid $(SCN)_2$ can be supercooled to -20° and then at -30° it solidifies.
2. Chemical.
   a. A solution of $(SCN)_2$ in ether or carbon disulfide (1) liberates iodine from iodides (7); (2) oxidizes copper from cuprous to cupric state (3, 4); (3) combines directly with metals; (4) reacts with mercury diphenyl to yield phenyl mercuric thiocyanate; (5) reacts with aniline to give p-thiocyanoaniline and aniline thiocyanate:



$$2C_6H_5NH_2 + (SCN)_2 = \text{(p-NCS-aniline)} + C_6H_5NH_2HSCN$$

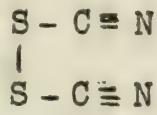
(6) reacts with unsaturated hydrocarbons to form addition products (3): $C_2H_4 + (SCN)_2 = C_2H_4(SCN)_2$; (7) aminolysis of thiocyanogen results in formation of compounds analogous to chloramines: $(SCN)_2 + 2NHR_2 = NCSNR_2 + NHR_2 \cdot HSCN$; (8) silver thiocyanate reacts with nitrosyl chloride to form nitrosyl thiocyanate; (9) reacts directly with mercuric cyanide to form a substance of composition CN(SCN) (4).

C. Formula.

In 1922 there was doubt as to the formula of thiocyanogen but Lecher and Gaebel determined the molecular weight of thiocyanogen and found that it corresponds to $(SCN)_2$ (9). In solutions of more than one normal, there exist higher polymers.

D. Structure.

It has been proposed that thiocyanogen exists in two tautomeric forms (3).



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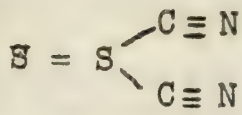


II

The evidence obtained by Mario Strada by his x-ray studies of thiocyanates, supports the first structure (9). He found the three atoms in a thiocyanate ion are arranged in a straight line. This is the structure suggested by Soderback.

V. Selenocyanogen $(SeCN)_2$.

A. Preparation.

1. Selenocyanogen has been prepared by Birckenbach and Kellerman by the electrolysis of potassium selenocyanate in alcoholic solution (1). They also prepared it by the action of iodine on silver selenocyanogen.

$$2AgI + (SeCN)_2 \rightleftharpoons 2AgSeCN + I_2$$

2. Kaufmann and Kögler prepared selenocyanogen (10) by the reaction of lead tetracetate in chloroform and potassium selenocyanate in dry acetone. The lead tetraselenocyanate decomposes to give selenocyanogen.

B. Properties.

1. Physical. Selenocyanogen is a homogeneous yellow powder and soon turns red in color. It is stable if dry and kept in a vacuum.

2. Chemical.

Selenocyanogen decomposes in water to form a mixture of H_2SeO_3, HCN, HSeCN.

$$2Se(CN)_2 + 3HOH = H_2SeO_3 + 3HSeCN + HCN$$

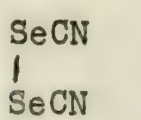
Selenocyanogen and carbon disulfide react when heated to form $Se_3(CN)_2$ and $Se(CN)_2$.

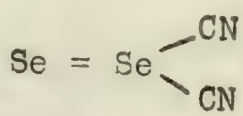
C. Formula.

Molecular weight determinations in benzene indicate that the formula is $(SeCN)_2$ (3). Determinations in glacial acetic acid indicate that $(SeCN)_2$ dissociates, maybe forming the unsaturated radical.

D. Structure.

1. Tautomeric forms (3).





2. Linear structure (11).

Pierre Spacu in the study of the Raman spectrum KSeCN, found that the frequency corresponds to the vibration of C≡N, and concluded that the formula of selenocyanate is N≡C-Se. Also selenocyanate is isosteric with Br-C≡N and since this is linear, one might expect selenocyanate to be linear.

VI. Oxycyanogen $(OCN)_2$.

A. Preparation (1, 12).

1. Potassium cyanate reacts with a neutral (25) solution of hydrogen peroxide, cupric oxide or sodium hypobromite to form oxycyanogen.

$$2KCNO + 2H_2O_2 = 2K_2CNO_2 + (CNO)_2 + 2H_2O$$

2. Nitrogen dioxide can be reduced by carbon at 150° to oxycanogen.
3. Cyanogen bromide reacts with silver oxide to give oxycyanogen.

B. Properties

1. Physical.

$(CNO)_2$ is a gas, lighter than carbon dioxide and may be present in human exhalation.

2. Chemical.

Oxycyanogen (a) liberates iodine from potassium iodide, (b) reacts directly with copper, zinc and iron, (c) forms interhalogenoid and halogen halogenoid compounds (13), (d) gives a white precipitate with a solution of barium hydroxide, and (e) is believed to be the anhydride of oxanic acid, H_2CNO_2.

C. Formula and structure.

Little work on the formula and structure has been done. According to Lidor, two isomeric oxanes may be obtained by varying the conditions or procedure.

α oxane β oxane

VII. Azidocarbon disulfide $(SCSN_3)_2$.

A. Preparation.

1. $(SCSN_3)_2$ may be prepared by chemical oxidation of azide dithiocarbonates such as $KSCSN_3$ by H_2O_2, KIO_3, K_2CrO_4, $HgCl_2$, $FeCl_3$, $KMnO_4$, MnO_2, Cl_2, I_2 and Br_2 (14, 15). The best procedure uses the reaction of a solution of iodine in potassium iodide on a solution of potassium azidodithiocarbonate.
2. $(SCSN_3)_2$ may also be prepared by the electrolytic oxidation of a solution of $KSCSN_3$.

B. Properties.

1. Physical.

$(SCSN_3)_2$ is a white unstable crystalline solid which is slightly soluble in water. It is very sensitive to both shock and impact.

2. Chemical.(14).

a. $(SCSN_3)_2$ reacts slowly with dilute acids and rapidly with concentrated acids, liberating sulfur. Nitric acid reacts but no sulfur precipitates.

b. $(SCSN_3)_2$ reacts with alkali in a manner similar to that of chlorine at -10°C.

$(SCSN_3)_2 + 2KOH = KSCSN_3 + KOSCSN_3$.

On acidification:

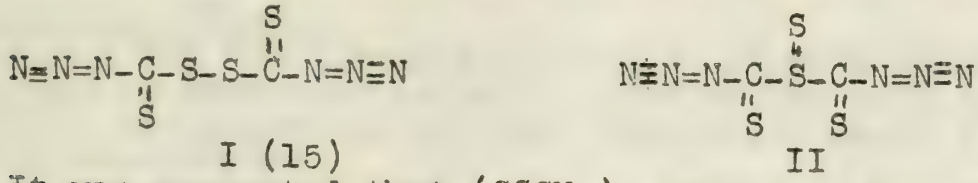
$KSCSN_3 + KOSCSN_3 + H_2SO_4 = K_2SO_4 + (SCSN_3)_2 + H_2O$

c. There is some indication that $KOSCN_3$ is converted to chlorate analog of azido carbon disulfide.
$3KOSCSN_3 = 2KSCSN_3 + KO_3SCSN_3$

d. $HSCSN_3$ is an acid comparable to H_2SO_4 in strength. ($K = 2.14 \times 10^{-2}$). This acid is stronger than HF, HCN and NH_3 and weaker than HCl, HBr and HI.

C. Formula and structure.

Browne and coworkers confirmed the formula $(SCSN_3)_2$.



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It was suggested that $(SCSN_3)_2$ exists in two tautomeric forms, but Browne believes the first structure to be the correct one.

VIII. Cyanogen $(CN)_2$ (16).

A. Preparation.

1. $(CN)_2$ is prepared by the thermal decomposition of $Hg(CN)_2$.
2. It can be prepared also by reaction of KCN on $CuSO_4$.
3. It can also be prepared by the dissociation of AgCN.

B. Properties.

1. Physical.

Vapor density is 2.321 g/l at 19.4° and 316.6 mm. pressure. The boiling point is -21.17° and the melting point is -27.9°C. It is a colorless gas, with a distinctive odor, very poisonous and it is soluble in water.

2. Chemical.

In alkaline solution it hydrolyzes to cyanide and cyanate. It decomposes in sunlight forming ammonium oxalate, ammonium formate and urea.

C. Structure and formula.

The formula of cyanogen has been shown to be $(CN)_2$.

Cyanogen at first was believed to have a ring structure but after much spectroscopic and electron diffraction work evidence has shown that the structure is $N \equiv C - C \equiv N$. The parachor and small dipole moment seem to uphold this structure (16).

IX. Azide (N_3^-).

The preparation of the free azide has not as yet been accomplished although Browne has attempted several times to isolate it (17).

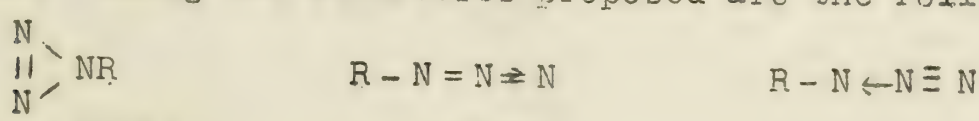
The radical has many properties similar to those of halogens.

A. Chemical properties.

1. Silver salts are insoluble.
2. Mixed halogenoids may be prepared.
3. Azides show absorption in the near ultra-violet region similar (18) to iodine.

B. Structure

Much research has been done on the structure of the azide ion. Among the structures proposed are the following:



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The ring structure was supported by Lindemann and Thiele, who obtained parachors corresponding to ring structure, and by Hantsch who based his studies on spectroscopic absorption. The linear structures are supported by Sidgwick and Freud. Sidgwick bases his proposed structure on heats of combustion and low dipole moments (20,21).

X. Tellurocyanogen $(TeCN)_2$.

Birckenbach and Kellermann attempted to prepare $(TeCN)_2$ by the electrolysis of KTeCN in alcoholic solution but were unsuccessful (1). Little investigation has been made since those first attempts to isolate the radical.

XI. Fulminate ion.

Only a few experiments on the fulminate ion have been tried thus far. Birckenbach and his coworkers have attempted to study it but with little success (3).

XII. Polyhalogenoids.

Several polyhalogenoids have been prepared and their properties studied. Included are $K(SeCN)I_2$, $K(SeCN)_2I$, $K(SeCN)_3$, $Cs(SeCN)_3$ (3).

XIII. Interhalogen-halogenoids.

The literature lists a large number of such compounds. Included are the following:

A. Azides.

Chlorazide, ClN_3 (22,23); bromazide, BrN_3 (24); and iodoazide IN_3 (24).

B. Cyanogen compounds.

Cyanogen chloride, CNCl; cyanogen bromide, CNBr, and cyanogen iodide, CNI. (16, 25).

C. Thiocyanogen compounds: thiocyanogen chloride, SCNCl; thiocyanogen trichloride, $SCNCl_3$; thiocyanogen monbromide, SCNBr; thiocyanogen tribromide, $SCNBr_3$ (26,27).

D. Azido-carbondisulfide compounds.

$Cl \cdot SCSN_3$, $BrSCSN_3$ and Br_3SCSN_3 may exist (28).

E. Oxycyanogen compounds: iodoxycyanate, ICNO (13); bromoxycyanate OCNBr.

XIV. Interhalogenoids.

Recent work in the halogenoid field has been devoted almost exclusively to the study of the structure of halogenoids and interhalogenoid compounds.

Among the interhalogenoid compounds studied are the following: cyanazide, CNN_3 (24), cyanogen thiocyanate $(CN \cdot SCN)$, cyanogen selenocyanate (10, 27); cyanogen azidodithiocarbonate $CN \cdot SCSN_3$ (27), thiocyanogen azidodithiocarbonate $SCN \cdot SCSN_3$ (14)

Recently Birckenbach and his coworkers have tried to extend the term "halogenoid" to include many inorganic radicals including many divalent radicals.

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University of Illinois
Urbana, Illinois
June 28, 1945

Dear Friends:

Enclosed are the seminar outlines for the last part of the school year which has just closed. We hope that you have found the series of interest and of value. If you wish to be continued on the subscription list next fall, please let us know. We want to continue sending the outlines to everyone who wishes them, but we do not wish to waste paper and postage by sending them to those who find them of no value. Subscriptions will be continued only to those who express a desire for continuance. You will be interested to know that the outlines have been mailed this year to fifty people, most of them alumni of the department. We shall be glad to extend the list to others who are interested.

Your suggestions on the seminar and the outlines have been greatly appreciated. Some of them have been put into effect; others will be utilized when times are more normal. We shall welcome further suggestions at any time.

The state legislature is still considering the biennial budget, but it is probable that money will be appropriated for a new building for Chemistry and Chemical Engineering. This is to be built across Mathews Street from the Chemistry Annex; the present plan is to design it for the use of the Divisions of Chemical Engineering, Organic Chemistry and Biochemistry and the administrative offices. The East half of Noyes Laboratory will be retained for the Divisions of Analytical Chemistry and Physical Chemistry, the Chemistry Library, the State Water Survey, and the General Chemical Stores. The top floor of the Chemistry Annex will be remodelled for the advanced work in Inorganic Chemistry. The West half of Noyes Laboratory will be converted into class rooms for other departments.

The University enrollment last year was about six thousand; plans for the fall term contemplate eight thousand. Summer enrollment is twenty-seven hundred. There are about seventy graduate students in chemistry, the majority of whom are devoting full time to government research. Most of the remainder are women; there are six discharged veterans. Unless the Selective Service regulations are changed, graduate enrollment will remain low for several years, as very few men are even finishing the undergraduate curriculum now.

Several of our staff are still on leave for war work. Professors Adams and Keyes are in Washington, and Dr. Deem is in the Army and is stationed at Edgewood Arsenal. Three members of the Inorganic Staff are in the Army--Professor Audrieth, who is directing research at Picatinny Arsenal, Dr. Nicholson, in the Chemical Warfare Service at Edgewood Arsenal, and Dr. Schirmer, commanding troops in Europe.

Professor Hopkins continues chemical work with his usual vigor and can be found in his office nearly any day. Mrs. Hopkins has been of invaluable help to the Department in the Army Specialized Training Program and the Navy V-12 Program.

With best wishes, I am

Sincerely yours,

John C. Bailar Jr.

John C. Bailar, Jr.

JCB/pf